

5120 – Advanced Metallics Branch – Highlights – FY01

- The superalloys Inconel-718 and Mar-M247 have been successfully cast in the Lattice Block structure, including architectures that contain an integral face sheet. Mechanical testing of ligaments machined from the lattice, as well as complete lattice blocks, has shown that the Lattice Block materials are very robust. (Hebsur, Whittenberger, Krause)
- Low Plasticity Burnishing (LPB) has been developed as an improved method for surface enhancement of metallic materials. It can produce a layer of compressive stress of high magnitude and depth, with minimal plastic deformation. The high cycle fatigue lives of Ni-base superalloys increased by 2-5X with the application of LPB, even when given simulated foreign object damage. (Gabb, Telesman)
- In Computational Materials Science, the BFS method has been extended to include 22 elements in 17 different AB-type compounds. The site occupancy predictions in each of the compounds was analyzed and compared with available experimental data, and has confirmed the robustness and accuracy of the methodology. (Bozzolo, Noebe)
- In collaboration with Solar Turbines, the fatigue durability of powder metallurgy U720 was determined. Notch-rupture sensitivity, fatigue and dwell crack growth were quantified and incorporated in the design and life prediction of turbine disks used in their land and sea-based turbines. (Gabb, Telesman)
- The feasibility of component fabrication methods for a new bimetallic rocket combustion chamber concept has been demonstrated. The combustor takes advantage of the conductivity and heat resistance of NiAl as an inner layer, and relies on an outer layer of superalloy for damage tolerance. (Gayda)
- Provided mechanical data and analysis for the redesign of a space power Stirling engine heater head for use in long-duration space missions. Extensive in-house creep testing combined with literature data was used to develop a probabilistic life model for the heater head. It was concluded that the design life of 100,000 hours could not be met with sufficient confidence. Since the operating conditions and mission profile could not be altered, it was necessary to redesign the heater head wall geometry in a manner that would lower the operating stresses without unduly sacrificing engine performance. (Bowman)

- Heat treatments to minimize residual stresses in advanced superalloy turbine disks were developed in parallel with efforts to develop a methodology for predicting stresses and subsequent machining distortions. The heat treatments and the predictions were verified on full-scale forgings. (Gayda)
- The design envelope for using low-density, high-stiffness cast g-TiAl alloys in low-pressure turbine blade applications has been determined. Six different factors that can effect damage tolerance and high cycle fatigue lives have been quantified on several commercial alloys. (Draper, Lerch, Pereira, Miyoshi)
- An extensive mechanical and physical properties design database for GRCop-84 was completed, and the work confirmed that the attractive properties of the alloy are maintained in commercial scale product. The alloy has been baselined in the 2nd Gen RLV program. (Ellis, Yun, Lerch, Garg, Ogbuji, Raj)

Analytical Science Group FY01 Highlights

Over 4666 Samples Analyzed in FY'01 (FY'00 4387)

CHEM	X-RAY	METLAB	SEM	PROBE	TEM
457 (573)	722 (628)	1829 (1853)	698 (748)	66 (32)	894 (553)

- ASG Customer Survey provided valuable feedback, ratings were 4+ out of 5 for 85% of the ratings.
- Direct XRF analysis of $\text{ZrO}_2/\text{Y}_2\text{O}_3$ TBC's as-sintered disks and coatings on metal substrates. (Nesbitt/Halloran)
- Verification of the composition of MX-4 master melt from PCC prior to casting of single crystal superalloys, analysis by ICP emission. (MacKay/Johnson)
- Over 700 carbon nanotube samples examined in SEM and TEM. (Chen/McCue/Hull)
- Tripod preparation and TEM investigation of microstructure of R&D 100 Award winning ceramic materials system and in situ-BN coated SiC/SiC composites. (Chen/Bansal/Yun))
- Tripod preparation and TEM investigation of microstructure of fiber, preform and composite after various high temperature treatments. (Chen/Bhatt/Thomas-Ogbuji)
- TEM investigation of nano-onion, nano-structure of carbon graphic shells. (Chen/VanderWal/Tomasek)
- Microstructure-mechanical property correlation in bond-coated advanced turbine blades. (Garg, Locci, Ritzert, MacKay)
- Fractography and microstructural analysis of GRCop-84 for 2nd Generation RLV applications. (Garg, Lerch, Ellis)
- Identification of salt-like impurities in graphite for Space Shuttle booster separation motor nozzles. (Hull)

2001 Highlights – Ceramics Branch 5130

- **Improved Constituents and Processes Developed for SiC/SiC Hot Section Components:** Several advances were made in the UEET program during 2001 to develop a SiC/SiC CMC with 2400°F temperature capability. Advances include outside debonding of BN interphase, fabrication of CMC's with higher CVI SiC content, thermal annealing of SiC-coated preforms to over 3000°F prior to melt infiltration and use of low ends per inch fabric. These improvements have resulted in 10X improvements in creep rupture life (compared to 9/99 EPM material) at 2400°F under stresses typical of combustor liner operating conditions. **(Jim DiCarlo (5100), Ram Bhatt, Greg Morscher, Janet Hurst, Hee Mann Yun (5120), and Linus Thomas-Ogbuji (5160)).**
- **Elevated Temperature Deposited Si-Doped BN Interphases Improves Durability of SiC/SiC Composites:** Melt-infiltrated SiC/SiC composites with high-temperature Si-doped BN interphases were fabricated on single pieces of fabric by Synterials Inc. These pieces of fabric were then stacked and fabricated into MI composites. The composites fabricated with Sylramic-iBN interphases had excellent stress-strain behavior at room temperature and improved 815°C stress-rupture behavior when compared to conventional BN, inside-debonding interphase composites. Most impressive was that very little interphase oxidation occurred during 815°C stress rupture compared to the significant oxidation that normally occurs for conventional BN interphase composites. **(Greg Morscher, Frances Hurwitz, and Hee Mann Yun, (5120))**
- **Outside Debonding of BN Interphases Improves Durability of SiC/SiC Composites:** A novel fiber-matrix interface control approach, called “outside debonding” has improved durability by at least an order of magnitude and significantly improved the strain-to-failure of silicon carbide fiber reinforced silicon carbide (SiC/SiC) ceramic matrix composites (CMCs) for gas turbine combustor liner and vane applications. Debonding at the fiber-matrix interface ahead of an advancing crack is critical for graceful failure in all CMC's. In the outside debonding approach, the fiber coating for SiC/SiC CMC's has been modified so that debonding occurs at the coating-matrix interface, instead of the commonly used approach of debonding at the fiber-coating interface. This restricts direct access of oxidizing gases to the fiber surface and, therefore, prevents strength loss and catastrophic failure associated with the formation of a glassy oxidation product next to the fiber surface. Recently, Goodrich Corporation, which is one of the two major SiC/SiC CMC manufacturers in the country, has proposed collaborating with GRC (Space Act Agreement) to further develop and scale up the outside debonding approach for commercial applications. **(Greg Morscher)**

- **Pulsed Chemical Vapor Infiltration (CVI) Technique Developed to Apply Si-Doped BN Coatings on Woven SiC/SiC Fabrics:** Si-Doped BN fiber coatings offer the potential for increasing durability of SiC/SiC CMC's. A computer-controlled, pulsed CVI System has been developed to deposit si-doped BN fiber coatings into 2-D woven ceramic preforms. This technique has demonstrated that BN fibers coatings with silicon content in the range of 6-24 atomic percent and low oxygen can be applied onto woven preforms. This is in contrast to the conventional CVI process in which the maximum si-dopant range is less than 5% and there is a significant oxygen level in the coating. **(Fran Hurwitz)**
- **Interlaminar Strengths of SiC/SiC CMC's Measured at High Temperature From C-Coupon Studies:** A "C-Coupon" was used to measure the interlaminar tensile behavior of five different composite materials: Sylramic/MI (melt infiltration SiC matrix), ZMI/MI, Sylramic/S300, and ZMI and Hi-Nicalon with an S200 matrix at room temperature, 816⁰C and 1204⁰C. The C-Coupon geometry employed here produced interlaminar fracture, as characterized by a series of primarily parallel cracks through the thickness of the specimen and following the "C" curvature, consistent with the location of maximum radial stress predicted by finite element analysis. Fracture primarily occurred between the BN and CVI interphase layers for the Sylramic/MI material, and the fiber and BN in the ZMI/MI composite. There was good agreement between the maximum radial stress at failure in the C-Coupon and the interlaminar tensile strength as determined from the "button test". **(Fran Hurwitz, A. Calomino, (5920) G. Morscher, T. McCue (5120))**
- **Melt Infiltrated SiC/SiC CMC Can Be Potential Candidate for Space Propulsion Applications:** Longer rupture lifetimes and superior creep rates were demonstrated for Melt-Infiltrated Silicon Carbide/Silicon Carbide composites relative to C/Silicon Carbide composites. This suggested that MI SiC/SiC may compete successfully in earth-to-orbit rocket applications where C/SiC is currently being investigated for use. MI SiC/SiC was developed by NASA's EPM and UEET programs for civil aviation engine use at high temperature applications up to 1315⁰C and for thousands of hours. It has been suggested that use temperatures in excess of 1400⁰C may not be plausible for this material due to the presence of molten free silicon at those temperatures. However, recent data demonstrates much higher use temperatures (1400⁰C and 1500⁰C) is clearly possible for MI SiC/SiC composites with longer lifetimes than for C/SiC. **(Janet Hurst)**

- **Durability of C/SiC CMC Improved By Using Alternate Carbon Fiber and Multilayered Fiber Coatings:** Initial stressed oxidation studies indicate that a carbon fiber reinforced silicon carbide (C/SiC) ceramic matrix composite (CMC) incorporating IM7 carbon fiber and a multilayer fiber coating has a longer life at 1200°C than standard C/SiC composites reinforced with the T-300 carbon fibers (the current carbon fiber of choice). Composite life was increased by a factor of approximately 2.5. Additional C/SiC composite specimens containing the IM7 fiber will be tested at higher temperatures (both with and without protective surface coatings that will further increase specimen life). Optimization of the fiber coatings could also provide further improvements in the material. (Jeanne Petko, Doug Kiser)
- **Oxidation Kinetics Models of Carbon Fibers in a Cracked Silicon Carbide Matrix Verified:** The oxidation kinetics of carbon fibers in a cracked silicon carbide matrix were verified by conducting stressed oxidation tests at 800°C and 1200°C in air and oxygen environments. Also, the experimental tests showed the significant effect cracks and stress had on the oxidation of carbon in the matrix. At high temperatures and/or low stresses, the cracks were closed and the composite became self-protected. At low temperatures and/or high stresses, the cracks were open and the carbon fibers were susceptible to oxidation through oxygen ingress through the cracks. A physics based finite difference oxidation model was run for the same temperatures and environments as in the experimental tests. The model gave the same oxidation trends and comparable times for oxidation as obtained experimentally. At 800°C, reaction controlled kinetics were observed where the oxidation process was controlled by carbon and oxygen reactions at the carbon surface and oxidation was observed throughout most of the modeled region from the edge to the interior. At 1200°C, the model showed diffusion-controlled kinetics which were controlled by the supply of oxygen. The model showed a sharp reaction front that moved inward as the outer layer of carbon fibers were consumed. The oxidation model proved to be a useful tool for studying the effect of certain variables (i.e. reaction rate, diffusion coefficient, environment, crack opening, temperature) on the oxidation process and the related kinetics. (Michael C. Halbig)

- **Cooled Ceramic Matrix Composite Panels Successfully Tested in Quartz Lamp Facility:** Ceramic matrix composite cooled panels have been tested in a joint NASA GRC/United Technologies Research Center program. This is a major technological milestone toward the future use of ceramic composite in the 3rd Gen. Reusable Launch Vehicle program. A series of 1"x 6" water-cooled ceramic matrix composite (CMC) heat exchangers have been successfully tested in a quartz lamp facility. This series of tests experimentally determined the thermal contact resistance for various types of interface materials, which were placed between the metallic coolant tubes and the ceramic matrix composite. These tests provided critical data for validating heat transfer models that were used to predict the minimum interfacial contact necessary to maintain allowable hot wall surface temperatures for the CMC panel. The results from this recent test, along with the validated models, will be used to design larger (up to 6" x 30") cooled CMC heat exchanger panels for testing in a rocket combustion rig under high heat flux conditions and in a scramjet rig. (M. Jaskowiak)
- **Ceramic Matrix Composite Thrustcells Successfully Hot-Fire Tested in Rocket Combustion Facility:** A series of cooled and uncooled ceramic matrix composite (CMC) thrustcells were successfully hot-fire tested in Cell 22 of the Rocket Combustion Lab at GRC. The testing program was part of a joint effort between NASA Glenn and NASA Marshall to develop light weight CMCs for high temperature space applications. Regeneratively cooled carbon/carbon and SiC/SiC CMCs were supplied by Ceramic Composites, Inc. and Hyper-Therm, Inc. The uncooled CMC thrust cells, which were fabricated by Ultramet, were ultra-high temperature carbide based CMCs. The focus of this effort was on the screening of CMC material capabilities as well as evaluation of thermal barrier coating performance. The CMC thrusters were tested with gaseous O₂/H₂. Maximum internal wall temperatures measured in-situ exceeded 4700°F for successful runs. For repeated 30 second runs on a single part, the maximum internal wall temperature was approximately 4300°F (M. Jaskowiak).

- **Structural Integrity of CMC Combustion Chamber Demonstrated During Hot-Fire Testing in Rocket Combustion Facility:** Ceramic matrix composite combustion chamber sub-components have been successfully tested under rocket firing conditions in a joint NASA GRC/MSFC/BOEING Rocketdyne program. This test represents a major technological advance toward the development of ceramic matrix composites (CMC) combustion chamber for the 3rd Generation Reusable Launch Vehicle Project. Coaxial CMC tubes were hot-fire tested at 10-second intervals in GRC's rocket combustion facility, with chamber pressures ranging from 100 to 1000 psi. The tests demonstrated that the hot rocket combustion gases could be contained inside the CMC combustion chamber without permeating through the CMC walls. The tests also demonstrated structural integrity of CMC combustion chamber under rocket firing conditions. **(Jerry Lang)**
- **Ceramic Propellant Injectors Designed and Fabricated:** Ceramic propellant injectors offer the potential for order-of-magnitude weight reductions in comparison to conventional metallic injectors and may enable some NASA missions. Injectors constructed of ceramic materials have the inherent advantages of being lighter weight, more erosion resistant, and capable of higher temperature operation than current metallic designs. The use of ceramics may facilitate new designs for a broad range of combustion devices in aero and space applications. In a joint project involving the Ceramics and Combustion branches, and Case Western Reserve University, a number of rocket propellant injector faceplates have been designed and fabricated using laminated object manufacturing and standard ceramic processing. A number of faceplates have been successfully hot-fire bench tested. **(Andy Eckel)**
- **Ultra High Temperature Ceramics Assessed For Reusable Propulsion Applications:** An assessment of zirconium diboride based ultra high temperature ceramics (UHTC) for a reusable propulsion application was completed. Silicon nitride was used as a reference material. The study determined that the UHTC have oxidation rates 3 to 4 orders of magnitude greater than Si₃N₄, and thermal shock resistance significantly less than Si₃N₄. Thus zirconium diboride and similar hafnium diboride UHTCs are not suitable for reusable propulsion applications. Studies are continuing to improve the oxidation resistance of UHTC materials. **(Stan Levine, Beth Opila (5160), Mike Halbig, Doug Kiser, Jay Singh, and Jon Salem, (5920))**

- **Rapid Prototyping of Ceramics Developed to Fabricate Silicon Nitride Vane:** GRC and Case Western Reserve University researchers have developed a rapid prototyping capability for fabrication of monolithic ceramics such as alumina and silicon nitride. Starting with a CAD file of the part to be made, permanent and removable mold components for gel casting of ceramic slips were made by stereolithography and Sanders machines, respectively. The gel cast part was dried and sintered to final shape. In fabrication trials, integrated core-shell forms were produced and used to mold an alumina gelcasting slurry to fabricate a simulated vane. Comparison of the cross section of the fabricated vane with the original CAD file outline confirmed that the fabrication process faithfully reproduced the original design and in particular, the narrow features in region of the trailing edge. Currently, this process is being extended to fabricate silicon nitride vanes with complex cooling hole geometry. **(Ram Bhatt, Jim Cawley)**

- **Directionally Solidified $\text{Al}_2\text{O}_3/\text{Er}_3\text{Al}_5\text{O}_{12}$ Fibers Offer Significant Increase in Creep Resistance Compared to Sapphire Fiber:** The microstructure and high temperature deformation characteristic of directionally solidified $\text{Al}_2\text{O}_3/\text{Er}_3\text{Al}_5\text{O}_{12}$ fibers with hypo-eutectic composition were studied between 1350°C and 1600°C at constant load. This eutectic system has a unique cellular microstructure with high aspect ratio (up to 100), Al_2O_3 cells and $\text{Er}_3\text{Al}_5\text{O}_{12}$ or $\text{Al}_2\text{O}_3/\text{Er}_3\text{Al}_5\text{O}_{12}$ eutectic boundaries. The $\text{Al}_2\text{O}_3/\text{Er}_3\text{Al}_5\text{O}_{12}$ system has a very high creep resistance, comparable to c-axis sapphire. Dislocation plasticity is suggested as the most plausible deformation mechanism. **(Ali Sayir, J.M. Fernandez)**

- **Mechanisms of High Temperature Creep Resistance and Strength of Directionally Solidified $\text{Al}_2\text{O}_3/\text{ZrO}_2(\text{Y}_2\text{O}_3)$ Eutectic Understood:** The eutectic architecture of a continuous reinforcing phase within a higher volume fraction phase or matrix, can be described as a naturally occurring in-situ composite. Studies were conducted to identify the sources of high temperature creep resistance and high levels of strength in a two phase $\text{Al}_2\text{O}_3/\text{ZrO}_2(\text{Y}_2\text{O}_3)$ system. The mechanical properties of two phase $\text{Al}_2\text{O}_3/\text{ZrO}_2(\text{Y}_2\text{O}_3)$ eutectic are superior to that of either constituent alone due to strong constraining effects provided by the coherent interfaces and microstructure. The $\text{Al}_2\text{O}_3/\text{ZrO}_2(\text{Y}_2\text{O}_3)$ eutectic maintains a low energy interface resulting from directional solidification and can produce strong and stable reinforcing phase/matrix bonding. The phases comprising a eutectic are thermodynamically compatible at higher homologous temperatures than man-made composites and as such offer the potential for superior high temperature properties. **(Ali Sayir, Serene Farmer)**

- **Strength and Fracture Toughness of Solid Oxide Fuel Cell (SOFC) Electrolyte Material Improved:** Recently conducted research has resulted in the improvement of strength and fracture toughness of SOFC electrolyte through the addition of alumina. SOFCs are being developed for various applications in the automobile, power generation, and aeronautic industries. More recently, NASA is exploring the possibility of using SOFCs for aero-propulsion under its Zero Carbon Dioxide Emission Technology (ZCET) Project. Yttria-stabilized zirconia (10YSZ) is a very good anionic conductor at high temperatures, and is therefore used as an oxygen solid electrolyte in SOFC. However, it has high thermal expansion coefficient, low thermal shock resistance, low fracture toughness and poor mechanical strength. For aeronautic applications, the thin ceramic electrolyte membrane of the SOFC needs to be strong and tough. We have demonstrated that the addition of alumina to zirconia electrolyte increases its strength as well as its fracture toughness. Flexure strength (s_p) and fracture toughness (K_{IC}) of the various zirconia-alumina composites showed systematic improvement with amount of alumina addition at room temperature and at 1000 °C. Use of these modified electrolytes, with improved strength and fracture toughness, should prolong the life and enhance the performance of SOFC in aeronautics and other applications. **(Narottam Bansal and Sung Choi, (5920))**

- **Additives Improve Processability of Candidate high temperature piezoelectric material:** Lanthanum Titanate has been shown to have potential as a high temperature piezoelectric. However this highly refractive oxide compound must be consolidated at relatively high temperatures. In addition, previous work on this material has revealed a time dependent deconsolidation after processing. Consolidation aids can reduce the processing temperature and possibly prevent post-processing deconsolidation. Additions of yttrium oxide as low as 1mol % prevented post-processing deconsolidation lanthanum titanate of with resulting densities of 5.3 grams per cubic centimeter with a reduction of 200°C in hot pressing temperature. This material exhibits extremely low mechanical heat dissipation and hence has mechanical fatigue resistant properties at low strains. Both the electrical and mechanical relaxations appear to be thermally activated processes. Additions of yttrium oxide increase the impedance as well as the a.c. frequency sensitivity. **(Jon C. Goldsby)**

- **Method Developed to Reduce Number of Lead Wires in Thermocouple Array Assemblies Used For Test Rig Instrumentation:** There is a need to reduce the number of lead wires and hence mitigate against thermocouple failure and to reduce the cost of using precious metals in the use and construction of thermocouple arrays. A method was developed to create a common ground leg to reduce the amount of precious metal wire used by 50%. Reduction in the number of leads also reduces the number of inputs needed for data acquisition. The thermocouples, which result from this method take up less surface coverage with no compromise in the amount of transmitted data. The system will work with large or small diameter wire as well as with thin-films. In each case the thermocouple beads will independently register an EMF, which is indicative of the temperature at that point. The filed disclosure for this method was selected to appear in a future edition of NASA Tech Briefs. (Jon C. Goldsby)
- **Affordable, Robust Ceramic Joining Technology (ARCJoinT) Technology Transferred to Trex Enterprises, Lihue:** Silicon carbide-based ceramics are widely used in electronic industries for various components in wafer fabrication systems. Trex Enterprises is actively involved in fabrication of silicon carbide tubes by CVC process for chemical delivery systems. The affordable, robust ceramic joining technology, which was developed in-house, was successfully transferred to Trex Enterprises, Lihue under a reimbursable space act agreement for the fabrication of ceramic components in electronic industry applications. (M. Singh and Rich Dacek)
- **Environment-Conscious Ceramics (Ecoceramics) Technology Winner of 2001 R&D 100 Award:** Environment-conscious ceramics are a new class of materials that can be fabricated with renewable resources (wood) and wood waste material (wood sawdust). Wood has been known to be one of the best and most intricate engineering materials created by nature and known to mankind. Environment-conscious ceramic materials, fabricated via the pyrolysis and infiltration of natural wood-derived preforms, have tailorable properties with numerous potential applications. The experimental studies conducted to date indicate that these materials behave like ceramic materials manufactured by conventional approaches. These bio-derived structures have been shown to be quite useful in producing porous or dense materials having various microstructures and compositions. (M. Singh and Rich Dacek)

Polymers Branch 2001 Major Technical Accomplishments

- Continue efforts to develop new polymeric materials with enhanced durability, processability and performance and reduced environmental, health and safety risks. These new polymers and composite materials prepared from them could find applications in aircraft engines, space transportation propulsion systems, and cryotanks for advanced space transportation vehicles. (W. Alston, K. Chuang, D. Hardy-Green, U.F. Ilhan, L. Inghram, C. Johnston, L. McCorkle, M. Meador, D. Papadopoulos, G. Roberts, D. Scheiman)
 - .. Resin Film Infusion (RFI) was used to prepare stitched carbon fiber composites from GRC developed HFPE polyimide by Boeing, Long Beach. These panels survived rapid heating (300°C/minute) to 400°C without delamination. Unstitched laminates usually delaminate at temperatures between 250 and 300°C. Because of the high glass transition temperature of the HFPE resin (>400°C), composites prepared from this resin have outstanding high temperature mechanical properties. Boeing is interested in evaluating these materials for aircraft and space transportation applications due to their high temperature performance and RFI processability. Resin Film Infusion can reduce manufacturing costs of composite components by about 30% and can enable the fabrication of large structures.
 - .. Completed initial imidization kinetics studies with various aromatic diamines in an attempt to correlate diamine reactivity with ¹⁵N nmr chemical shifts. Initial results suggest that diamines with similar ¹⁵N nmr chemical shifts have equivalent reactivities. If successful, this effort will lead to a quick technique to evaluate the reactivity of new experimentally developed diamines for use in polyimide synthesis and will provide valuable kinetic data that will aid in the processability of new high temperature polyimides.
 - .. Initiated a study to examine the effects of various substituents (electron donors and acceptors) on the processability, stability, and performance of polyimides derived from 4,4'-diaminotriphenylmethane. These diamines were prepared by Prof. John Droske, U of Wisconsin-Stevens Point under a collaboration with the Army and GRC.

- .. Completed preliminary static and high strain rate shear tests on polymer resin specimens at Ohio State University (NAG3-2522). Specimens were fabricated at NASA and supplied to OSU for testing. Both the brittle epoxy (E-862) and the toughened epoxy (PR520) showed a region of linear deformation at strains below 0.05 followed by a region of plastic deformation extending to strains greater than 0.2. At a strain rate of 700s^{-1} plateau stresses were about two times greater than the plateau stresses in the static tests. Initial moduli and strains at failure were also strongly dependent on strain rate. Further testing is in progress to optimize the specimen geometry and to examine the effect of test temperature. This information could find application in the design of efficient lightweight fan containment systems for aircraft engines and composite fan blades.
- .. Continued collaborations with Kent State University, Ohio Aerospace Institute, Drexel University and Adherent Technologies to develop electron beam curable polymers for use at temperatures up to 290°C . These efforts have led to new polymer blends (interpenetrating networks) that have glass transition temperatures as high as 330°C . Electron beam cured high temperature polymers would find application in cryogen fuel tanks for advanced space transportation systems and in propulsion (aircraft and spacecraft) components.
- .. Initiated new collaboration with Clark Atlanta University to evaluate RTM and VARTM processability of low melt viscosity polyimides developed by GRC and LaRC.
- .. Participated with Maverick Corporation, the Air Force Materials Lab, B.F. Goodrich, and GKN in a successful proposal to the State of Ohio's Technology Action Fund to develop and commercialize resin transfer moldable high temperature polymers. This activity enables GRC to leverage \$50K of R&D funds against a total state/federal government and industry investment of about \$1M to do research in this important area. GRC developed resins will be evaluated along with materials developed by the Air Force and Maverick.
- Utilizing nanotechnology to develop advanced polymeric materials for power and propulsion applications. This effort encompasses research in polymer/clay nanocomposites, carbon nanotubes and molecular self assembly. (S. Campbell, U.F. Ilhan, M. Lebron, M.Meador, D. Scheiman)

- .. Developed a new procedure to purify carbon nanotubes produced by investigators at Rice University using the HiPCO process. This purification procedure removes metal catalyst particles and carbon impurities and increases the onset of decomposition of the nanotubes from 300°C to over 600°C. Iron concentration in the purified tubes is reduced from 2.9% to 0.32%. These purified tubes were extensively characterized using thermal analysis, infrared and Raman spectroscopy.
- .. Demonstrated functionalization of carbon nanotubes through the formation of molecular complexes with pyrene derivatives. Other methods of nanotube functionalization involve chemical reactions with the nanotube and certain functionalizing agents. This changes hybridization of the carbons that react from sp^2 to sp^3 , thereby introducing defects into the nanotubes that could adversely affect their thermal and electrical conductivities, mechanical properties and stability. Formation of molecular complexes does not disrupt the hybridization of nanotubes. In addition the chemistry used to produce these nanotube complexes is simpler than other functionalization methods.
- .. Developed an organically modified silicate clay which on dispersion in a PMR-15 matrix, leads to a nanocomposite with up to a 12% increase in thermal oxidative stability. Utilization of this PMR-15 nanocomposite as a matrix in carbon fabric (T650-35) reinforced composite increases the composite thermal stability by 25% in comparison to a neat PMR-15 matrix composite. This increase in stability is achieved without any adverse effect on PMR-15 processability.
- .. Organically modified silicate/thermoplastic polyimide nanocomposites were prepared with improved solvent and moisture resistance and reduced hydrogen permeability. Moisture absorption is a problem with polyimides and can lead to blistering and delamination of composites at high temperatures. The absorption of acetone into the nanocomposite samples was decreased in comparison to the neat polymer by up to 47%, after 28 hours. In water, absorption was decreased by up to 22% after 32 hours. Hydrogen permeability testing of these materials results in up to a 20% decrease in permeability. The effectiveness of the nanocomposite in decreasing absorption or permeation was dependent on the silicate modification. These materials are being evaluated for use in composite tankage for hydrogen fuel for fuel cell powered vehicles and space transportation vehicles.

- .. Completed the synthesis of electron donor/acceptor substituted compounds which upon irradiation produce products which can self assemble into hydrogen bonded stacks. Efforts are underway to grow large crystals of these self-assembled stacks in order to confirm their supramolecular structure. To date, these efforts have produced fine needles that are too small for X-ray. Solid state charge transfer interactions in these compounds will be investigated.
- Continued collaborations with Environmental Durability Branch (5160) and the Electrochemistry Branch (5420) to develop and evaluate polymer electrolytes for lithium-polymer batteries and high temperature proton exchange membranes for fuel cells. (J. Kinder, M. Meador, J. Santos, D. Scheiman, M.A.B. Meador (5160))
 - .. Initiated efforts to develop new polymeric materials for use as proton exchange membranes for fuel cells. Design studies at GRC and elsewhere suggest that the optimum operating temperature for PEM fuel cells is around 130°C. Current materials (Nafion) are not suitable for use at temperatures above 80°C, due to poor high temperature stability and poor moisture retention (essential for good proton conductivity) at elevated temperatures. A series of sulfonated polyimide/ poly(ethylene oxide) rod-coil polymer have been developed that have undoped room temperature conductivities close to that of Nafion. Thermal analysis of films prepared from these systems suggests that they have better high temperature stability than Nafion and retain moisture better at high temperatures. Doping of these polyimides with phosphotungstic acid increases proton conduction and further increases moisture retention at temperatures as high as 150°C.
 - .. Developed a synthesis of novel discotic liquid crystalline electrolytes for lithium-polymer batteries. Completed initial thermal analysis of these compounds.
- Continued efforts to develop and transfer polymer technology to industry for use aircraft and space transportation propulsion components. (L. Inghram, J. Kinder, L. McCorkle, D. Papadopoulos, E. Shin, D. Scheiman, J. Sutter, J. Thesken (OAI/5920))
 - .. Continued collaboration with Rocketdyne to design, fabricate and test a high temperature polymer matrix composite component for space transportation propulsion system.

- ❑ Worked with materials suppliers (Maverick Corporation, Adherent), prepreg manufacturers (YLA), and composite fabricators (Boeing, Canyon Composites and Fiber Innovations) to develop new fiber treatment schemes, evaluate prepreg techniques, fiber architectures, and processing methods for production of high temperature composite test laminates.
 - ❑ Worked with the Air Force Materials Laboratory and 5920 to understand the effects of hygrothermal, exposures on the durability of high temperature composites and with Southern Research Institute to determine both the intrinsic and transient mechanical properties and the hygrothermal performance of these materials under the extreme rocket engine environments.
 - ❑ Developed test plan for design allowables for this component and completed Phase I of coupon testing plan. Initiated design and fabrication of subcomponents and developed test plan for these subcomponents.
- .. Continued collaboration with Allison Advanced Development Corporation and initiated new collaboration with Pratt and Whitney to demonstrate erosion resistant coatings for use with composite vanes.
 - ❑ Completed optimization of composition and processing parameters for Plasma Vapor Deposition of coatings at ECI.
 - ❑ Initiated optimization study for the production of coating system using Plasma Spray Deposition at GRC.
- .. In collaboration with GE, initiated efforts to evaluate the ballistic impact behavior of 3D braided composite panels and 44" diameter half-ring composite panels manufactured by A&P Technologies for use in aircraft engine containment systems fabricated using a low cost resin infusion process. Both toughened and untoughened resins were used to evaluate both material processing issues and impact performance. In addition, some panels were fabricated with a grid of stiffeners to control the size of the damage zone during impact and to limit post impact damage growth. Impact test data on these composite panels will provide critical data needed for materials selection and design optimization for a composite fan case.
- .. Initiated discussions with General Motors and the Army on potential collaborations in the development and evaluation of polymeric materials for fuel cell systems applications.

- Initiated new efforts in biotechnology with a focus on materials modeling and molecular sensors. (A. Freed, M. Meador)
 - “ Initiated a collaboration with the Cleveland Clinic Foundation to develop analytical models to permit surgeons to perform “virtual surgery” on patients using robots guided by surgeons. This work is funded by the Army.
 - “ Performed detailed photophysical characterization of a series of charge transfer fluorescent dyes being developed as molecular sensors for polymers and biological systems. The fluorescence behavior of these compounds is sensitive to their chemical environment. GRC has signed Space Act Agreements with two biomedical diagnostic companies to further develop these compounds for use as fluorescent tags for protein expression and drug screening and for medical diagnostic purposes.
- Upgraded Branch facilities and instrumentation to meet current and future programmatic needs (C. Johnston, J. Kinder, E. Shin)
 - Purchased and installed new atomic force microscope (Digital Instruments Nanoscope 4)
 - Designed and developed “High Energy High Density Infra-red Rapid Heating System with Controlled Cooling” in collaboration with Innovative Industries Inc to be used in in-service rapid heat-up (200°F/sec) simulation core programs. This system is capable of 200 ~ 400°F/sec heating rate up to 1000°F.
 - Updated AvPro processing control system for Polymers Branch Processing Labs, including replacement of existing computers, relocation of computers to avoid contamination from carbon fiber, and update of software.

Thanks to our TID Support Staff, Howard Eakin, John Juhas, Vic Klans, and Adrienne Veverka, and our Administrative Support Staff, Sandy Clay and Becky Shott (InDyne) for your efforts in supporting the Polymers Branch!

Environmental Durability Branch Technical Accomplishments in 2001

Aerospace Propulsion and Power Program

- Developed, tested and conducted parametric case studies of a user-friendly program to rapidly model cyclic oxidation weight change data. First introduction at the 2001 Gordon Conference on High Temperature Corrosion. “COSP for Windows – Strategies for Rapid Analyses of Cyclic Oxidation Behavior” to be published in Oxidation of Metals. Obtained software release and have sent 10 copies to interested organizations. (Smialek, Auping)
- Developed a new deterministic interfacial cyclic oxidation/spalling model (DICOSM). An approximation of Svi enabled closed-form algebraic expressions for incorporation into the model. (Smialek, Good, Auping)
- Thermogravimetric weight-loss studies of the stability of alumina in model combustion environments produced experimental measurements which closely agreed with predictions for the reaction $\text{Al}_2\text{O}_3 + 3 \text{H}_2\text{O(g)} = 2 \text{Al(OH)}_3\text{(g)}$, based on literature data. Mullite formed on the surface at 1500°C due to interactions with the fused quartz furnace tube and surface etching was seen due to the formation of volatile hydroxides. (Opila, Myers)
- Williams International has initiated manufacturing the EJ22 turboprop engine, a commercial version of the FJX-2 engine developed under NASA’s General Aviation Propulsion (GAP) Program. Eclipse Aviation, Inc. is creating an exclusive, six-seat aircraft priced at less than most used turboprops and powered by twin EJ22 turboprops. Collaborative research has continued via Mach 0.3 burner rig testing under simulated flight conditions. High-pressure EJ22 turbine blades of varying alloy chemistry, with a proprietary protective coating, have been exposed to 2000 hot hours to determine the influence of chemistry, temperature and thermal cycling on blade life. Results of the test exposures indicate exceptional blade life, lending support to continuing development of the EJ22. (Fox, Cuy)
- A refined design of a multiple cell flange for alloy activity measurements is nearing implementation completion. The design provides extremely accurate positioning of the standard and research specimen. Advances in temperature measurement accuracy have been implemented, however additional work to maintain temperature stability especially during stage movement is required. (Copland, Jacobson, Auping)

- Completed simple thermodynamic modeling of the ZrO₂-Y₂O₃-Yb₂O₃ system. The first approach treats each oxide as a 'unit'. A more sophisticated approach, now underway, will treat the ions and vacancies separately. (Jacobson)
- Demonstrated that high quality plasma-sprayed erosion-resistant coatings could be successfully applied to AE 3007 polymer composite inlet guide vanes. AADC will incorporate coated vane triplets into a scheduled engine rainbow test. Optimization of the plasma spray process has led to future erosion testing in gas turbine engine environments. (G. Leissler, Sutter)
- A substituted norbornene end cap was found to have similar cure properties to the parent end cap used in addition polyimides, such as PMR-15, but the new end cap ages in such a way as to lead to improved thermo-oxidative stability. Two patents issued recently for this and a related technology. (Meador)
- Synthesized a new series of rod-coil polyimides with glass transition temperatures around -50°C and room temperature conductivities as high as 3×10^{-5} S/cm, almost an order of magnitude better than state-of-the-art PEO. The films could be cast directly onto electrode substrates or handled as free standing films, offering flexibility in battery fabrication. (MAB Meador)
- RAC bond coat - Baseline and first advanced Pt-Aluminide bondcoat received from Howmet under Space Act Agreement and cyclic furnace tested to EB-PVD TBC failure. Cycle life comparisons were: Howmet baseline 274; Advanced 400, NASA baseline (NiCoCrAlY) on N5 188; NASA baseline on EPM alloy 121; NASA baseline on CMSX4 92; Hebsur bondcoats NiAl-AlN 68; NbCrAlWY 30. (Nesbitt, Barrett)
- Alloy Design Workbench (ADW) - A final suite of BFS-based Monte Carlo Fortran computer codes were completed and is now being integrated with a Java-based front-end that implements a graphical user interface. Components of the ADW were used to conduct a large-scale study of segregation in 42 BCC binary alloys. (Good)
- The High Pressure Burner Rig testing of GE disk materials to determine the role of carbon, effect of cycling, incubation period, pressure, and alloy chemistry on the corrosion rate of selected alloys has begun. Non-corrosive testing of a series of alloys (including some with proprietary coatings) were exposed at 1350F and 9 atm, providing baseline weight loss and dimensional change data. (Robinson)

- Demonstrated application of hybrid technique of optical profiler and stylus profiler to measure critical dimensions such as volume loss and depth of eroded craters with excellent precision and accuracy. (Miyoshi)
- The fretting behavior of gamma-TiAl in contact with Ni-based superalloy has been characterized. While fretting damage produced metallic and oxide wear debris, scratched and plastically deformed disparities, cracks and fracture pits, initial fatigue testing has indicated that the fretting damage is not severe enough to affect fatigue strength. (Miyoshi)
- Completed a total of 1200 hr pulsed laser-enhanced thermal fatigue test of HA188 tensile fatigue specimens. Oxidation and creep-enhanced fatigue at the oxide scale/alloy interface was an important mechanism for the experimentally observed surface crack initiation and propagation under the simulated a pulse detonation engine conditions. (Zhu, Fox and Miller)
- Formulated and successfully advocated 2 new research efforts: Lattice block fan blade design concepts and Effect of hot corrosion on the durability of advanced Ni-based superalloy disks. (Raj)
- Developed a new dislocation microstructure-based mesoscale model for creep. (Raj)

Ultra-Efficient Engine Technology Program

- Provided technical assistance to the Propulsion Systems Division of the Naval Air Station in Patuxent River, Maryland to bring a Becon burner rig into service. Advised on rig operations, combustor design, air and fuel controls, thermal cycling, thermocouple and pyrometric methods. (Cuy)
- Completed Mach 0.3 burner rig testing of new lead wire thermocouple attachment designs developed by the Sensors and Electronics Technology Branch. SiC/SiC panels incorporating a SiC-based cement, and an alumina-based flamed-sprayed coating, called Rokide, improved the performance of the lead wire to sensor transition. (Cuy)

- Determined optimum low conductivity composition ranges for both plasma-sprayed and EB-PVD new oxide clustered TBCs. (Zhu, Miller) Furnace cycle lives of low conductivity oxide clustered TBC indicate that coating life improvements have been realized through processing and compositional optimizations. (Nesbitt, Barrett, Zhu, Miller)
- Thermal cyclic behavior and failure mechanisms for the thermal and environmental barrier coating systems were identified. (Zhu, Lee, Miller)
- Identified EPM Environmental Barrier Coating upper use-temperature limit of 1400°C, based upon silica volatility, thermal conductivity, phase stability, and high steam thermal cycle test studies. Several promising 2700°F (1482°C) EBC candidates identified based on silica volatility, thermal conductivity, and high steam thermal cycle test. (Lee, Fox, Robinson, Zhu)
- Completed cyclic water vapor furnace and HPBR test matrix of Ames Research Center UHTC materials including HfB_2/SiC (HS), ZrB_2/SiC (ZS), and $\text{ZrB}_2/\text{C}/\text{SiC}$ (ZCS). Tests were conducted for 50 hrs at 1100 C, 1200 C, and 1300 C. HS materials showed slight wt gains with a k_p similar to furnace tests at 1100 C and total weight losses near 3% at 1300 C. ZS and ZCS materials produced powdered scales and significant weight loss at 1100 C, increasing to greater than 26% total weight loss along with glass formation at 1300 C. X-ray results indicated the same species (HfO_2 , HfSiO_4 , ZrO_2 , and ZrSiO_4) as in furnace testing. (Robinson, Nguyen, Opila)
- A procedure for computing the coefficient of thermal expansion via constant-pressure molecular dynamics simulation has been developed. To date, the process correctly predicts the ordering of the CTEs of several pure metals, but the magnitudes of the coefficients are off by about 50 percent on average. The accuracy of the technique will be improved when the BFS-based molecular dynamics code replaces the current Morse-potential-based code. (Good)
- Completed environmental exposures for determination of composites post-exposure mechanical properties of SiC/SiC designed to “outside-debond” (i.e. debonding and sliding between the BN interphase and the matrix). Properties were comparable to pre-exposure levels. (Thomas-Ogbuji, Morscher)

- A prototype feature testing specimen holder, which can accommodate tubes up to nearly 2.0" diameters, a test module allowing for impingement cooling and measurement of both external and internal temperatures, was designed/fabricated. The test holder/test module is easily accessible for inspection, weight change measurement, or specimen replacement. The tested tubes remained in place, both surface materials temperatures and internal cooling air temperatures were obtained, and the hardware appeared to have good durability. Internal cooling could be varied, flows measured and repeated, and the resulting temperatures of the surface and internal cooling air could be influenced by the flows. (Robinson, Verrilli)
- A test module was designed, fabricated, and used to successfully test six of the RQL Sector Rig (CE-9) lean transition liners in the HPBR. The test was conducted through 100 hrs and nearly 200 cycles. The baseline cycle adopted was a 30 min transient with 15 min of dwell time at approximately 2700F. All hardware survived intact with no major durability concerns, specifically to the impingement ring, which was fully instrumented. Access ports in both the main ring and impingement plates have since been added to accommodate both optical and fiber optic pyrometers to measure the backside temperature. (Robinson, Verrilli)
- A test module was designed/fabricated to evaluate an acoustic temperature measurement concept in which acoustically acquired isotherms are obtained in a duct carrying a hot, high velocity gas stream, using only the noise already present in the flow (developed by John Kleppe from the University of Nevada at Reno). Data reduction is underway at the university. (Robinson)
- Thermogravimetric analysis was conducted to determine effect of H₂O on advanced environmental barrier coatings at 2700 F. Of the fifteen oxides studied to date, three of the compositions were the most durable in a 50% H₂O - 50% O₂ environment and have been down-selected for more in-depth study. (Lee)
- Stress-rupture testing and thermogravimetric analysis was conducted on C/SiC specimens in air and steam-containing environments. The stress-rupture lives at 600°C were longer than the lives at 1200 °C and the average test duration in steam at 600°C was at least 30 times longer than the lives obtained in air. The 1200 °C data revealed little difference between lives of specimens tested in air and steam at atmospheric pressure. Little composite damage was observed for the specimen tested at 600 °C, while significant damage, in the form of carbon fiber oxidation, was evident at 1200 °C. (Verrilli, Opila, Kiser, Calimino)

- A laser high heat-flux rig, capable of monitoring thermal conductivity in real time, has been adapted for monitoring delamination crack propagation under realistic engine temperature and stress gradients. Delamination cracking, initiated within the test specimen by the introduction of a known-sized flaw, causes an apparent decrease in the measured thermal conductivity. By combining video, thermographic, and pyrometric measurements with modeling and theoretical analysis one may quantitatively evaluate the thermal fatigue and fracture behavior of ceramic thermal barrier coatings under steady state or cyclic exposure conditions. (Miller, Zhu)
- Early EPM studies indicated that hafnium (Hf) additions to a Pt-modified nickel aluminide bond coat on a superalloy component substrate were beneficial to the overall TBC durability. Cyclic furnace testing was undertaken to better understand the mechanism of the improvement and reproducibility of the effect. Hf additions were shown to increase the adherence of the thermally grown oxide and the Pt-NiAl bond coat, increasing TBC life by a factor of three. (Nesbitt)
- Process, heat transfer and fluid flow modeling: a. Predict temperature distribution in SiC diode; b. Predict heat transfer for current configuration and evaluate/recommend improved configurations for polymer compression molding tooling; c. Predict temperature distribution along a crack in a TBC and relate to thermographic measurements to determine crack dimensions. (Kuczmarski)

Space Transportation Projects

- Oxidation of T-300 carbon fibers in hydrogen/water vapor environments has been studied to predict the lifetimes of these fibers in ceramic matrix composites for space propulsion environments. Temperature dependence of the oxidation rate in water vapor was clarified and the velocity dependence was shown to agree with predictions. TGA has been modified for testing in water vapor/hydrogen mixtures, with high hydrogen contents, that are realistic models of fuel-rich rocket combustion environments. (Opila)
- HfB_2 -20 vol% SiC samples were oxidized in stagnant air at 1327, 1627, and 1927°C. Microstructural analyses and recession measurements for this material and ZrB_2 -20 vol% SiC were conducted. These Ultra-High Temperature Ceramics (UHTC's), are candidates for leading edges on re-entry vehicles and hot sections of short-term space propulsion applications. Recession rates were rapid, limiting these materials to very short-term use (minutes) in air at high temperatures. (Opila)

- Designed and procured a Quick Access Rocket Exposure (QARE) rig test-fire prototype. The rig will be capable of a low-pressure H_2/O_2 fueled, rich and lean gas mixtures, producing a heat flux >100 btu/in²-s, over a heated zone of 2-3" diameter. The test site (Bldg. 24, Cell 1) has been prepared, the safety permit process is underway, and the rig is expected to arrive in early March. (Robinson)
- A study of the stress-rupture behavior of C/SiC in various environments (air, vacuum, and steam) was conducted. Results revealed that presence of steam at low temperature (600 °C) resulted in 10X longer lives than obtained in air due to a reduced rate of oxidation of carbon fibers in water vapor. In contrast, rupture lives at 1200 °C in steam and air were similar. (Verrilli)
- To assess the condition of the SiC/SiC liners after combustor testing in the RQL sector rig, their mechanical properties were measured and NDE data was obtained. One component examined, the lean transition liners, were generally unaffected by the exposures of up to 260 hours. Post exposure strengths of the other component examined, the lean zone inner diameter liners, decreased with increasing exposure time. Thermography NDE techniques were able to image damage that occurred during combustor exposure. (Verrilli)
- Tensile strengths and stress-rupture lives were obtained for (C/SiC) composite specimens at 1200°C in an environment of 1000-ppm oxygen, with argon as the remaining gas. Plate-to-plate variability of tensile strength and stress-rupture lives was observed. During the stress-rupture testing of C/SiC specimens, the partial pressure of O_2 flowing out of the chamber was monitored and found to vary as a function of test time for any given test. Also, the effluent partial pressure of O_2 varied with test stress. (Verrilli)
- Oxidation studies of several Cu-based alloys are well underway in support of GRCop, and related Cu-based compositions, for application as rocket engines thrust cells. (Thomas-Ogbuji)
- Completed detailed research planning and selected vendor for optimization of low-pressure plasma sprayed overlay coatings for GRCop-84 RLV combustor liners. Several coating compositions are being studied for protecting from the blanching damage sometime seen in current materials. (Raj)
- The mysterious 'white deposit' appeared on the nose cap and wing leading edge—after three of the shuttle fleet had been exposed to rain was analyzed to be Na_2CO_3 . CO_2 and H_2O from rainwater and the atmosphere combine with the sodium silicate on the wing leading edge and nose cap to form Na_2CO_3 . This will be reproduced in the laboratory to assess the potential damage (if any) from this deposit. (Jacobson)

Rewards and Recognition

- EBC Patents: Silicon Based Substrate with Calcium Aluminosilicate Environmental/Thermal Barrier Layer – Technology,” US Patent No. 6,284,325 Sept. 4, (2001). “Silicon Based Substrate with Calcium Aluminosilicate Environmental/Thermal Barrier Layer – Fabricated Article,” US Patent No. 6,296,942 Oct. 2, (2001). “Silicon-Based Substrate with Yttrium Silicate Environmental/Thermal Barrier – Technology,” US Patent No. 6,296,941 Oct. 2, (2001). “Silicon-Based Substrate with Yttrium Silicate Environmental/Thermal Barrier - Fabricated Article,” US patent No. 6,312,763 Nov. 6, (2001). An additional six invention disclosures. (Lee, et al)
- K. Lee and W. Worrell, “High Temperature Alloys,” US Patent No. 6,127,047 Oct (2000).
- 2001 R&D 100 Award: “Silicon/Mullite/BSAS and Silicon / Mullite+BSAS / BSAS EBCs (Environmental Barrier Coatings).” (Lee, Smialek, Opila, Bansal, Robinson, Fox, Jacobson, Miller)
- US Patent 6,316,078 Segmented Thermal Barrier Coating J.L. Smialek, Nov. 13, 2001.
- Received TIGR Award for “Outstanding contributions to and exceptional progress toward the General Aviation Propulsion (GAP) Revitalization Team.”(Fox, Cuy)
- G. Leissler was invited by the American Society of Materials International to write technical workbook for the Practical Engineering Learning Series entitled “Safety, Handling and Documentation for Thermal Spray Processing,” published October 2001.
- Team Achievement Award for Source Evaluation Board supporting the Special Projects Office. (Fox)

Successful Techniques for Reducing Instabilities in Advanced Nickel-Base Superalloys For Turbine Blades

Rebecca A. MacKay, Ivan E. Locci, Anita Garg, and Frank Ritzert

The High Speed Research (HSR) Airfoil Alloy Program developed fourth-generation single crystal superalloys with up to a +85°F increase in creep rupture capability over current production airfoil alloys. Recent results have been obtained on these fourth-generation alloys, but in coated form, for subsonic turbine blade applications under the NASA UEET (Ultra Efficient Engine Technology) Program. A goal for the UEET Program is to optimize the airfoil alloy/thermal barrier coating system for 3100°F turbine inlet temperatures. The state-of-the art turbine blade airfoil system consists of a superalloy single crystal that provides the basic mechanical performance of the airfoil. A thermal barrier coating is used to reduce the temperature of the base superalloy, and a bondcoat is deposited between the base material and the thermal barrier coating. The bondcoat improves oxidation and corrosion resistance of the base superalloy, and improves the spallation resistance of the thermal barrier coating. A commercial platinum aluminide bondcoat was applied to the HSR-developed alloys, and a diffusion zone developed as a result of interaction between the bondcoat and the superalloy.

Optimized strength is obtained for superalloys when the refractory element content is high and the limits of microstructural stability are approached or exceeded slightly. In the case for the fourth-generation alloys, instability leads to the formation of topologically close packed (TCP) phases which form internally in the superalloy and a secondary reaction zone (SRZ) which forms under the diffusion zone. There was a concern that excessive quantities of either TCP or SRZ have the potential of decreasing the mechanical properties of the superalloy, with SRZ thought to be particularly detrimental and its formation unpredictable. Thus, an SRZ reduction effort was initiated in the NASA UEET Program so that methods developed during the HSR program could be optimized further to reduce or eliminate SRZ.

Secondary reaction zone is a three-phase constituent comprised of TCP and stringers of gamma phase in a matrix of gamma prime. An incoherent grain boundary separates the SRZ from the gamma-gamma prime microstructure of the superalloy. The SRZ is believed to form as a result of local chemistry changes in the superalloy due to the application of the diffusion aluminide bondcoat. Locally high surface stresses also appear to promote the formation of SRZ. Thus, techniques that change the local alloy chemistry or reduce surface stresses have been examined for their effectiveness in reducing SRZ. These SRZ reduction steps are performed on the test specimen or the turbine blade before the bondcoat is applied. Stress relief heat treatments have been demonstrated to reduce significantly the amount of SRZ that develops during subsequent high temperature exposures. Stress relief heat treatments reduce the surface stresses by recrystallizing a thin surface layer of the superalloy. However, in alloys with very high propensities to form SRZ, stress relief heat treatments alone do not eliminate SRZ entirely. Thus, techniques that modify the local chemistry under the bondcoat have been emphasized and successfully optimized at NASA Glenn. One such technique is carburization, which changes the local chemistry by forming sub-micron carbides near the surface of the superalloy. Detailed characterizations have demonstrated that the depth and uniform distribution of these carbides are enhanced when a stress relief treatment and an appropriate surface preparation are employed in advance of the carburization treatment. Even in alloys that have the propensity to develop a continuous SRZ layer beneath the diffusion zone, the SRZ has been completely eliminated or reduced to low, manageable levels when this combination of techniques is utilized.

Now that the techniques to mitigate SRZ have been established, TCP phase formation is being emphasized in on-going work. The limits of stability of the fourth-generation alloys, with respect to TCP phase formation, are currently being defined along with high temperature creep rupture properties. In addition, a regression model is being developed for the prediction of the presence of TCP phase in the microstructure and SRZ under the diffusion zone. The model is based on a design-of-experiments methodology with emphasis on the potential synergistic effects of alloying elements.

Cyclic Oxidation Modeling for *Windows*®

James L. Smialek Judith V. Auping

Turbine superalloy components are subject to high temperature oxidation during operation. Protection is often conferred by coatings designed to form slow-growing and adherent oxide scales. Degradation by oxidation is enhanced due to the thermal cycling encountered during normal aircraft operations. Cooling has been identified as the major contributor to stresses in the oxidation scales, and it may often cause some spalling with a proportional loss of protective behavior. Overall oxidation resistance is thus studied by weight change behavior of alloy coupons during high temperature cyclic oxidation in furnaces or burner rigs, and the various characteristics of this behavior are crucial in understanding the performance of alloys at high temperatures. This new modeling effort helps in the understanding of the major factors involved in the cyclic oxidation process.

Weight change behavior in cyclic oxidation is typified by an initial parabolic weight gain that eventually exhibits a maximum, then transitions into a linear rate of weight loss due to spalling. The overall shape and magnitude of the curve are determined by the parabolic growth rate, the cycle duration, the type of oxide scale, and the regular repetitive, spalling process. This entire process has been modeled by the computer program called COSP (Cyclic Oxidation Spalling Program) previously developed at GRC. Thus by inputting various appropriate oxidation parameters, the best fit to actual data can be determined. These parameters describe real behavior and can be used to compare alloys and project cyclic oxidation behavior for longer times or under different cycle frequencies.

This program has been re-written to run under a Windows operating system. This allows for some major benefits in navigating between various control screens as well as interfacing with other applications. Point-and-click operating features include multiple drop-down menus for setting the model input parameters, for importing experimental data for analysis, and to view quick, on-screen plots that show any of the six output parameters for up to 10 models. Families of model curves on the instant plot screen readily show the sensitivity to various input parameters and allow rapid and precise fitting to experimental curves. Five model curves are presented with various spalling parameters. One curve represents the best fit to the experimental data obtained for 1200°C cyclic oxidation of NiAl.

The program can be operated conveniently while other Windows applications remain open for importing experimental weight change data, storing model output data, or plotting of model curves in a graphics package. The program includes save and print options as well as a help file.

Along with the sample weight change, other salient terms are calculated – the existing scale weight and the cumulative amounts of oxygen consumed, metal consumed, and spall weight. These are all listed in a table accessed by the **Results window** button. Key descriptive parameters (such as the number of cycles to reach the maximum weight gain and to reach zero weight change, the final weight loss slope, and the plateau in oxygen gain), are all highlighted as part of a summary text output.

Robust, Durable TiAl Low Pressure Turbine (LPT) Blades

Susan L. Draper, Bradley A. Lerch, Kazuhisa Miyoshi, and J. Michael Pereira

g - TiAl is an attractive new material for aerospace applications due to its low density and high specific strength in comparison to currently used titanium and nickel-base alloys. However, this intermetallic is inherently brittle, and long life durability is a potential problem. As part of the aviation safety goal to reduce the aircraft accident rate, the potential for g - TiAl to be used for robust LPT blades has been thoroughly studied. The effect of impact damage and casting porosity on the fatigue life of cast Ti-48Al-2Cr-2Nb alloys was assessed. The Al content of TiAl can vary slightly due to the casting process and the effect of a lower Al content on the impact resistance and resulting fatigue strength was also studied. Ti-48Al-2Nb-2Cr is one of the original cast TiAl alloys to show promising mechanical properties. However, more recently developed alloys have been developed for enhanced mechanical properties. One of these alloys, ABB-2, has a much higher strength but only half the ductility of Ti-48Al-2Nb-2Cr. The ballistic impact resistance and remnant fatigue strength of ABB-2 was determined and compared to Ti-48Al-2Nb-2Cr. Additionally, the effect of fretting damage on the fatigue life of cast Ti-48Al-2Nb-2Cr was studied.

Ballistic impacts resulted in two forms of cracks, the severity of which depended on impact energy. At lower impact energies, the specimens failed in fatigue from the backside cracks that were perpendicular to the specimen axis. At higher impact energies, the fatigue failure initiated from the Hertzian cracks on the frontside of the specimen. Hertzian and backside crack lengths were similar for a particular impact condition for both the high and low Al content Ti-48Al-2Nb-2Cr alloys as well as the ABB-2 alloy. Defect size played a large role in determining the critical fatigue loads. Increasing the defect size, regardless of whether the flaws resulted from casting porosity or from impact cracks, led to a decrease in the fatigue strength according to the $a^{-0.5}$ relationship described by fracture mechanics. The fatigue strength of Ti-48Al-2Nb-2Cr and ABB-2 showed a similar dependence on external crack length and this was due to the fact that both materials had the same fatigue threshold stress intensity. Therefore, to improve damage tolerance, an alloy with a higher fatigue threshold is required. Within the limits of the test program, the fatigue strength of Ti-48Al-2Nb-2Cr was not affected by fretting damage indicating its excellent fretting resistance. The synthesis of the entire data set on impact, chemistry, processing, fatigue and fretting has demonstrated that TiAl has sufficient durability to allow design of a robust low pressure turbine blade.

Evaluation of Ti-48Al-2Cr-2Nb Under Fretting Conditions

Miyoshi, K., Lerch, B.A., Draper, S.L., and Raj, S.V.

Material parameters govern many of the design decisions in any engineering task. When two materials are in contact and microscopically small, relative motions (either vibratory or creeping) are occurring, fretting fatigue can result. Fretting fatigue is a material response influenced by the materials in contact as well as such variables as loading and vibratory conditions. Fretting produces fresh, clean interacting surfaces and induce adhesion, galling, and wear in the contact zone. Time, money, and materials are unnecessarily wasted when galling and wear result in excessive fretting fatigue and will lead to poorly performing and unreliable mechanical systems.

Fretting fatigue is a complex problem of significant interest to aircraft engine manufacturers. Fretting failure can occur in a variety of engine components. Numerous approaches, depending on the component and the operating conditions, have been taken to address the fretting problem. The components of interest in this investigation were the low-pressure turbine blades and disks. The blades in this case were titanium aluminide, Ti-48Al-2Cr-2Nb, and the disk was a nickel-base superalloy Inconel 718 (superalloy 718). A concern for these airfoils is the fretting in fitted interfaces at the dovetail where the blade and disk are connected. Careful design can reduce fretting in most cases, but not completely eliminate it, because the airfoils frequently have a skewed (angled) blade-disk dovetail attachment, which leads to a complex stress state. Further, the local stress state becomes more complex when the influence of the metal-metal contact and the edge of contact is considered.

The fretting behavior of Ti-48Al-2Cr-2Nb (g-TiAl) in contact with the nickel-base superalloy 718 was examined in air at temperatures from 296 to 823 K (23 to 550 °C). All fretting wear experiments were conducted at loads from 1 to 40 N, frequencies of 50, 80, 120, and 160 Hz, and slip amplitudes between 50 and 200 μ m for 1 million to 20 million cycles. The interfacial adhesive bonds between Ti-48Al-2Cr-2Nb and superalloy 718 were generally stronger than the cohesive bonds within Ti-48Al-2Cr-2Nb. The failed Ti-48Al-2Cr-2Nb was transferred to the superalloy 718 at all fretting conditions, such that from 10 to 50 percent of the superalloy 718 contacting surface area became coated with the Ti-48Al-2Cr-2Nb. The maximum thickness of the transferred Ti-48Al-2Cr-2Nb was approximately 20 μ m. In reference experiments Ti-6Al-4V transferred to superalloy 718 under identical fretting conditions. Compared with Ti-48Al-2Cr-2Nb transfer, the degree of Ti-6Al-4V transfer was greater, such that from 30 to 100 percent of the superalloy 718 contacting surface area became coated with the Ti-6Al-4V. The thickness of the transferred Ti-6Al-4V ranged up to 50 μ m. The wear scars produced on Ti-48Al-2Cr-2Nb contained metallic and oxide wear debris, scratches, plastically deformed asperities, cracks, and fracture pits. Although oxide layers readily formed on the Ti-48Al-2Cr-2Nb surface at 823 K, cracking readily occurred in the oxide layers both within and around the contact areas. The wear volume loss of Ti-48Al-2Cr-2Nb generally decreased with increasing fretting frequency. The increasing rate of oxidation at elevated temperatures led to a drop in wear at 473 K. Mild oxidative wear and low wear volume were observed at 473 K. However, fretting wear increased as the temperature was increased from 473 to 823 K. At 723 and 823 K, oxide film disruption generated cracks, loose wear debris, and pits on the Ti-48Al-2Cr-2Nb wear surface. Both increasing slip amplitude and increasing load tended to produce more metallic wear debris, causing severe abrasive wear in the contacting metals.

Major Effects of Non-metallic Inclusions on Fatigue Life of Disk Superalloy Demonstrated

T. P. Gabb, J. Telesman, P. T. Kantzos, P. J. Bonacuse, R. L. Barrie

The fatigue properties of modern powder metallurgy disk alloys can vary due to the different steps of materials/component processing and machining. Among these variables, the effects of non-metallic inclusions introduced during the powder atomization and handling processes have been shown to significantly degrade low cycle fatigue life. The levels of inclusion contamination have therefore been reduced to less than 1 part per million in state-of-the-art nickel disk powder processing facilities. Yet large quantities of compressor and turbine disks weighing from 100 to over 1000 pounds do have enough volume and surface area for these rare inclusions to still potentially be present and limit fatigue life. The objective of this study was to investigate the effects on fatigue life of these inclusions, as part of the Crack Resistant Disk Materials task within the Ultrasafe program. Inclusions were carefully introduced at elevated levels in a nickel-base disk superalloy, U720, produced using powder metallurgy processing. Multiple strain-controlled fatigue tests were then performed on extracted test specimens at 650°C. Analyses were performed to compare the LCF lives and failure initiation sites as functions of inclusion content and fatigue conditions.

Powder of the nickel-base superalloy U720 was atomized in argon at Special Metals Corporation, Inc. using production-scale high cleanliness powder processing facilities and handling practices. The powder was then passed through a 270 mesh screen. One portion of this powder was set aside for subsequent consolidation without introduced inclusions. Two other portions of this powder were “seeded” with alumina inclusions. Small, polycrystalline soft (“Type 2”) inclusions of about 50 microns diameter were carefully prepared and blended into one powder lot, while larger hard (“Type 1”) inclusions of about 150 microns mean diameter were introduced into the other seeded portion of powder. All three portions of powder were then sealed in separate containers, hot isostatically pressurized, extruded, forged into subscale disks, and heat treated. Low cycle fatigue specimens were then extracted, machined, and tested. Fatigue tests were performed at 650°C in closed-loop servo-hydraulic testing machines using induction heating and axial extensometers. All tests were continued to failure, and fractographic evaluations were performed on all specimens to determine the crack initiation sites.

A large majority of the failures in specimens with introduced inclusions occurred at cracks initiating from inclusions at the specimen surface. The inclusions significantly reduced fatigue life from unseeded material levels. These effects were found to be dependent on strain range, strain ratio, and inclusion size. Tests at lower strain ranges and higher strain ratios produced larger effects of inclusions on life. Inclusion effects on life were thereby maximized in tests at the lowest strain range of 0.6% and most positive strain ratio of 0.5. In these conditions, small Type 2 inclusions substantially reduced life by about 20X, while large Type 1 inclusions dramatically reduced life by 100X. These results clearly demonstrated that it is essential to include the effects of inclusions on life for realistic predictions of disk fatigue life. Important issues concerning inclusion effects which include temperature dependence, crack initiation versus propagation, surface treatments, realistic disk features and machining, and realistic disk spin testing will be addressed in order to accurately model inclusion effects on disk fatigue life.

DUAL MICROSTRUCTURE HEAT TREATMENT OF A NICKEL-BASE DISK ALLOY

John Gayda

Gas turbine engines for future subsonic aircraft will require nickel-base disk alloys with temperature capability in excess of 1300F. Smaller turbine engines, with higher rotational speeds, also require disk alloys with high strength. To address these challenges NASA funded a series of disk programs in the 1990's. Under these initiatives, Honeywell and Allison, focused their attention on Alloy 10, a high strength, nickel-base disk alloy, developed by Honeywell for application in small turbine engines used in regional jet aircraft. Since tensile, creep, and fatigue properties are strongly influenced by alloy grain size, the effect of heat treatment on grain size and the attendant properties were studied in detail. It was observed that a fine grain microstructure offered the best tensile and fatigue properties, while a coarse grain microstructure offered the best creep resistance at high temperatures. Therefore, a disk with a dual microstructure, consisting of a fine grained bore and a coarse grained rim, should have high potential for optimal performance.

Under NASA's Ultrasafe and UEET Projects, a disk program was initiated to assess the feasibility of producing a dual microstructure disk using Alloy 10. The objectives of this program were twofold. First, existing Dual Microstructure Heat Treatment (DMHT) technology would be applied and refined as necessary for Alloy 10 to yield the desired grain structure in full-scale forgings appropriate for use in regional gas turbine engines. Second, key mechanical properties from the bore and rim of a DMHT Alloy 10 disk would be measured and compared to "conventional" heat treatments to assess the benefits of DMHT technology.

Four full scale Alloy 10 disks were converted to a dual grain microstructure using an active cooling DMHT process. The fine grain size in the bore can be contrasted with the coarse grain size in the rim. Testing of coupons machined from these disks showed the DMHT approach did indeed produce a high strength, fatigue resistant bore and a creep resistant rim. This combination of properties was previously unobtainable using "conventional" heat treatments, which produced disks with a uniform grain size.

Future plans are in place to spin test a DMHT disk under the Ultrasafe Project to assess the viability of this technology at the component level. This testing will include measurements of disk growth at high temperature as well as determination of burst speed at intermediate temperature.

Understanding the Oxidation Behavior of GRCo-84

Linus U. Thomas-Ogbuji

NASA's goal of safe, affordable space transportation calls for increased reliability and lifetimes of launch vehicles, and a significant reduction of launch costs. The areas targeted for enhanced performance in the next generation of Reusable Launch Vehicles (RLVs) include combustion chambers and nozzle ramps, therefore the search is on for suitable liner materials for these components. GRCo-84 (Cu-8Cr-4Nb), an advanced copper alloy developed at NASA Glenn Research Center in conjunction with Case Western Reserve University, is a candidate. The current liner of the space shuttle main engine is another copper alloy, NARloy-Z (Cu-3Ag-0.1Zr), and it provides a benchmark against which to compare the properties of candidate successors.

The thermomechanical properties of GRCo-84 have been shown to be superior, and its physical properties comparable, to those of NARloy-Z. However, environmental durability issues control longevity in this application: because copper oxide scales are not highly protective, most copper alloys are quickly consumed in oxygen environments at elevated temperatures. In consequence, NARloy-Z and most other copper alloys are prone to blanching, a degradation process that occurs through cycles of oxidation-reduction as the oxide is repeatedly formed and removed due to micro-scale fluctuations in the oxygen-hydrogen fuels systems of rocket engines. The space shuttle main engine lining is typically degraded by blanching-induced hot spots that lead to surface roughening, pore formation, and coolant leakage. Therefore, resistance to oxidation and blanching are key requirements for second-generation RLV liners. The rocket engine ambient includes H_2 fuel and H_2O (combustion product), and is hence under reduced oxygen partial pressures. Accordingly, our studies were expanded to include oxygen partial pressures as low as 322 parts-per-million (ppm) and at temperatures likely to be experienced in service.

In 2.2% and higher oxygen content, GRCo-84 oxidation is slower than those of NARloy-Z or Cu, but that advantage is lost or diminished in 322 ppm O_2 . Over longer (50-hour) exposures in 1.0 atm O_2 , however, the advantage of GRCo-84 increased significantly, its oxidation rate becoming approximately ten times slower than those of Cu and NARloy-Z from 500 to 700°C. Weight gains are moderate and the kinetics parabolic for all 3 materials in 2.2% and higher oxygen content; however, in 322 ppm O_2 the scales are non-protective below about 650°C, as reflected in linear kinetics and large weight gains. The superior oxidation resistance of GRCo-84 is likely related to the kinetics of extra oxygen consumption to form the additional oxides of Cr and Nb detected beneath the GRCo-84 oxide layer.

While we continue to evaluate the blanching resistance of GRCo-84 in other tests, these oxidation results indicate that GRCo-84 is suitable as RLV liner, and in applications where it is desired to use a copper alloy but without the risk of oxidative failure.

Effects of Microalloying on the Microstructures and Mechanical Properties of Directionally Solidified Ni-33(at.%)Al-31Cr-3Mo Eutectic Alloys

J. Daniel Whittenberger, Sai V. Raj, Ivan E. Locci and Jonatham A. Salem

Despite an attractive combination of oxidation and thermo-physical properties, the development of nickel aluminides (NiAl) alloys as replacements for superalloy airfoils in gas turbine engines has been largely limited by the difficulty in developing alloys with an optimum combination of high elevated temperature creep resistance and room temperature fracture toughness. Although single crystal and polycrystalline NiAl alloys with superior specific creep strengths, comparable or better than advanced superalloys, were developed by a combination of alloying and innovative processing techniques in the mid-1980's to mid-1990's, these materials possessed poor room temperature fracture toughness restricting their induction into service. Alternatively, research has focused on developing directionally-solidified (DS) NiAl-based in-situ eutectic composites consisting of the NiAl and the (Cr,Mo) phases in order to obtain a desirable combination of properties. Recently, it has been demonstrated that the room temperature fracture toughness, K_{IC} , of the DS Ni-33 (at.%)Al-31Cr-3Mo two-phase eutectic alloy is about $17 \text{ MPa m}^{0.5}$. This is a considerable improvement over that of NiAl for which $K_{IC} \sim 6 \text{ MPa m}^{0.5}$. However, the elevated temperature strength of this DS eutectic alloy is still less than that of advanced nickel-based superalloys.

A systematic investigation was undertaken to examine the effects of small additions of eleven alloying elements (Co, Cu, Fe, Hf, Mn, Nb, Re, Si, Ta, Ti and Zr) in amounts varying from 0.25-1.0 at.% on the elevated temperature strength and room temperature fracture toughness of DS Ni-33Al-31Cr-3Mo eutectic alloy. The alloys were grown at 12.7 mm/hr, where the unalloyed eutectic base alloy exhibited a planar eutectic microstructure. The additions of these elements even in small amounts resulted in the formation of cellular microstructures, and in some cases, dendrites and third phases were observed. Most of these elemental additions did not improve either the elevated temperature strength or the room temperature fracture toughness over that of the base alloy. However, small improvements in the compression strength were observed between 1200 and 1400 K when 0.5% Hf and 0.25% Ti were added to the base alloy. The results of this study suggest that microalloying of Ni-33Al-31Cr-3Mo will not significantly improve either its elevated temperature strength or its room temperature fracture toughness. Thus, any improvements in these properties must be acquired by changing the processing conditions.

Long-Term Creep Assessment of a Thin-Walled Inconel 718 Stirling Power-Convertor Heater Head

Randy Bowman

DOE and NASA have identified Stirling power convertors as candidate power supply systems for long-duration, deep space science missions. A key element for qualifying the flight hardware is long-term durability assessment for critical hot section components of the power convertor. One such critical component is the power convertor heater head. The heater head is a high-temperature pressure vessel that transfers heat to the working gas medium of the convertor, which is typically helium. An efficient heater head design is the result of balancing the divergent requirements of thin walls for increased heat transfer, versus thick walls to lower the wall stresses and thus improve creep resistance/durability. In the current design, the heater head is fabricated from the Ni-base superalloy Inconel 718.

Although IN-718 is a mature alloy system, there is little long-term (>50,000 hours) creep data available for thin-specimen geometries. Since thin-section properties tend to be inferior to thicker samples, it is necessary to generate creep data using specimens with the same geometry as the actual flight hardware. Therefore, one facet of the overall durability assessment program involves generating relatively short-term creep data using thin specimens at the design temperature of 649°C (1200°F).

Based on more than 63,000 hours of cumulative creep testing, combined with metallurgical analysis, materials research efforts at NASA Glenn have resulted in a heat treatment and microstructure that optimizes the creep behavior of thin sheets of the nickel base superalloy IN-718. For instance, creep testing of thin samples with various grain sizes provided data that allowed a determination of the ideal grain size for this application. The ideal size was determined by balancing the opposing needs of, on one hand, having large grains so as to maximize creep life while, while on the other hand, avoiding the mechanical property debit associated with large grains which arises when there are too few grains through the wall thickness.

The overall life prediction methodology consists of generating a material-specific database for the Stirling power converter application, defining the appropriate definition of failure, developing a probabilistic design methodology, and verifying the critical flight hardware using benchmark tests. Final validation of the flight hardware design will be accomplished by calibrating/verifying the life models using benchmark tests on actual heater heads under prototypical operating conditions.

Creep life predictions, based on existing literature data combined with the in-house test results of the actual flight hardware material, have indicated that the heat treatment and microstructural optimization efforts have increased the expected life from approximately 60,000 to near 80,000 hours. Unfortunately, given the present operating conditions, even the optimized material will not achieve the goal of 100,000-hr life. Based on the results of the material analysis, modifications to the heater head geometry have been suggested that would allow the optimized material to achieve the desired mission life.

NEW HIGH-PERFORMANCE SiC FIBER FOR CERAMIC COMPOSITES

James A. DiCarlo and Hee Mann Yun

Sylramic-iBN fiber is a new type of small-diameter (10 mm) SiC fiber that was developed at NASA Glenn and was recently selected as an RD-100 product for the year 2001. It is produced by subjecting commercially available Sylramic™ SiC fibers, fabrics, or preforms to a specially designed high-temperature treatment in a controlled nitrogen environment for a specific time schedule. It can be used in a variety of applications, but currently has greatest advantage as reinforcement for SiC/SiC ceramic composites that are targeted for long-term structural applications at temperatures higher than the capability of metallic superalloys.

The commercial Sylramic™ SiC fiber, which is the precursor for the Sylramic-iBN fiber, is produced by Dow Corning. It is derived from polymers at low temperatures and then pyrolyzed and sintered at high temperatures using boron-containing sintering aids. The sintering process results in very strong fibers (>3 GPa), which are dense, oxygen-free, and nearly stoichiometric. They also display an optimum grain size that is beneficial for high tensile strength, good creep resistance, and good thermal conductivity. The NASA-developed treatment allows the excess boron in the bulk to diffuse to the fiber surface where it reacts with nitrogen to form an *in-situ BN* coating on the fiber surface (thus the product name of Sylramic-iBN fiber). The removal of boron from the fiber bulk allows the retention of high tensile strength while significantly improving creep resistance and electrical conductivity, and probably thermal conductivity since the grains are slightly larger and the grain boundaries cleaner. These improvements allow the fiber to display the best rupture strength at high temperature in air for any available SiC fiber. In addition, for CMC applications under oxidizing conditions, the formation of an in-situ BN surface layer creates a more environmentally durable fiber surface not only because a more oxidation-resistant BN is formed, but also because this layer provides a physical barrier between contacting fibers with oxidation-prone SiC surface layers.

NASA Glenn has demonstrated that the in-situ BN treatment can be simply applied to Sylramic™ fibers located within continuous multi-fiber tows or within woven fabric pieces, or when assembled into complex product shapes (preforms). SiC/SiC ceramic composite panels have been fabricated from Sylramic-iBN fabric and then tested at NASA Glenn within the Ultra Efficient Engine Technology (UEET) program. The test conditions were selected to simulate those experienced by hot-section components in advanced gas turbine engines. The test results at NASA demonstrated all the benefits expected for the Sylramic-iBN fibers. That is, the composites displayed the best thermostructural performance in comparison to composites reinforced by the Sylramic™ fibers and by all other currently available high-performance SiC fiber types. For these reasons, the UEET program has down-selected the Sylramic-iBN fiber for on-going efforts aimed at SiC/SiC engine component development.

IMPROVED ARCHITECTURES FOR HIGH PERFORMANCE CERAMIC COMPOSITES

Hee Mann Yun and James A. DiCarlo

A major thrust of the Ultra Efficient Engine Technology (UEET) Program at NASA Glenn is to develop advanced hot-section engine components using SiC/SiC ceramic matrix composites (CMC) with thermostructural capability to 2400°F (1315°C). In previous studies, UEET has determined that the higher the ultimate tensile strength (UTS) of the as-fabricated CMC, the greater the structural capability of the CMC at 2400°F. Thus efforts have been on going within UEET to understand and develop fiber architecture approaches that can improve the UTS of SiC/SiC CMC.

Under UEET, SiC/SiC test panels and demonstration engine components are currently produced by the multi-ply lay-up of two-dimensional (2D) fabric pieces. To form the fabric, multifilament tows containing high-performance Sylramic™ SiC fiber from Dow Corning are typically woven into 2D five harness satin (5HS) fabric with 20 ends per inch (epi) in the 0- and 90-degree directions. In some cases, fabric pieces containing woven Sylramic fiber tows are thermally treated at NASA to form Sylramic-iBN fibers that contain a very thin in-situ grown BN (boron nitride) layer on their surfaces. The final SiC/SiC panels and components are fabricated at the CMC vendor by compressing the fabric pieces in tools and then depositing a thin BN interphase coating on the fibers by chemical vapor deposition (CVI). The last step at the vendor is to infiltrate the BN-coated fiber architecture with SiC and silicon matrix constituents in order to form a dense product.

Because the as-produced Sylramic fiber tows are sized with a thin polymer coating for facilitating handling and weaving, the individual fibers within the tows and fabric are in close contact with each other. This contact is further increased during fabric compression. One important recent finding is that increasing Sylramic fiber tow width in a fabric increases the UTS of the final SiC/SiC CMC. This effect is presumably related to minimizing fiber/fiber contact, which can be detrimental to CMC strength due to the boron-rich chemistry and roughness of the Sylramic fiber surface. Tow spreading can be performed by mechanically agitating the Sylramic fabric prior to CMC fabrication or by simply thermally treating the Sylramic fabric as in the formation of the Sylramic-iBN fibers. However, CMC with the treated Sylramic-iBN fabric are even stronger than CMC with mechanically spread Sylramic tows. The extra strength capability is presumably related to the in-situ BN on the fiber surface, which adds compliance to the fiber surfaces and is more resistant to oxygen impurities introduced during the CVI BN process.

Another important finding is that use of fabric with tow ends-per-inch less than the standard of 20 epi can provide advantages in terms of reduced ply height and increased ply and CMC strength. The reduced ply height provides more control of part thickness by allowing more plies for a given thickness and by reducing interlaminar residual stresses between plies. The increased ply strength is presumably related to a reduced number of interlaced 90-degree tows, which in turn reduces the crimp angle on the high-modulus fibers in the 0-degree tows. Although fabric with lower epi reduced the maximum fiber fraction in an 8-ply CMC panel, CMC UTS actually increased due to increased ply strength. Thus using fabric with low epi has various advantages, including providing a significantly higher strength per fiber fraction in the CMC. Thus on-going UEET efforts will attempt to use architectural approaches for components that minimize fiber-fiber contacts and fiber bending within the final composite microstructure.

Mechanical Properties of Directionally Solidified $\text{Al}_2\text{O}_3/\text{ZrO}_2(\text{Y}_2\text{O}_3)$ Eutectics

S.C. Farmer and A. Sayir

Oxide eutectics offer high temperature strength retention and creep resistance in oxidizing environments. Al_2O_3 - ZrO_2 eutectic strengths have been studied since the 1970's. Directionally solidified oxide eutectics exhibit improved resistance to slow crack growth and excellent strength retention at high temperatures up to 1400 °C. Materials studied typically contain Y_2O_3 to metastably retain the high temperature cubic and tetragonal polymorphs at room temperature.

Substantial variations from the eutectic alumina to zirconia ratio can be tolerated without a loss in room temperature strength. The effect of increasing Y_2O_3 addition on the room temperature tensile strength of an Al_2O_3 - ZrO_2 material containing excess Al_2O_3 was examined. Al_2O_3 - ZrO_2 is of fundamental interest for creep studies as it combines a creep resistant material, Al_2O_3 , with a very low creep resistance material, ZrO_2 . Results on mechanical properties and microstructures of these materials will be used to define compositions for creep testing in future work.

The Al_2O_3 - $\text{ZrO}_2(\text{Y}_2\text{O}_3)$ materials proved highly tolerant of growth defects maintaining an average strength of 1 GPa in the presence of 1 to 2 micron pores and large shrinkage cavities, which extend with crack-like morphology along the fiber axis. Critical defects were external facets, intercolony pores and other stress concentrators contained within the low toughness Al_2O_3 phase that is in residual tension. Future studies will concentrate on strengthening the Al_2O_3 phase and increasing the amount of crack deflection experienced at the Al_2O_3 - ZrO_2 interfaces through use of dopants to achieve a combination of high strength and an acceptable toughness.

Single Crystal Elastic Constants of Yttria (Y_2O_3) to High Temperatures

J. W. Palko, W. M. Kriven, S.V. Sinogeikin, J. D. Bass, and A. Sayir

Yttria, or yttrium sesquioxide (Y_2O_3), has been considered for use in nuclear applications and has gained interest relatively recently for use in infrared optics. Single crystal of yttria has successfully been grown using laser heated float zone technique in a fiber and rod. Such samples allow measurement of the single-crystal elastic properties and these measurements provide useful property data for the design of components using single crystals. They also yield information as to what degree the elastic properties of yttria ceramics are a result of the intrinsic properties of the yttria crystal as compared to characteristics that may depend on processing such as microstructure and intergranular phases, which are common in sintered yttria. The single-crystal elastic moduli are valuable for designing such optical components. In particular, the temperature derivatives of elastic moduli allow dimensional changes due to heating under physical constraint, as well as acoustic excitation to be determined.

The single-crystal elastic moduli of yttria have been measured by Brillouin spectroscopy up to 1200 °C. The room temperature values obtained are $C_{11} = 223.6 \pm 0.6$ GPa, $C_{44} = 74.6 \pm 0.5$ GPa, and $C_{12} = 112.4 \pm 1.0$ GPa. The resulting bulk and (Voigt-Reuss-Hill) shear moduli are $K = 149.5 \pm 1.0$ GPa and $G_{\text{VRH}} = 66.3 \pm 0.8$ GPa, respectively. Linear least squares regressions to the variation of bulk and shear moduli with temperature result in derivatives of $dK/dT = -17 \pm 2$ MPa/°C and $dG_{\text{VRH}}/dT = -8 \pm 2$ MPa/°C. Elastic anisotropy was found to remain essentially constant over the temperature range studied.

Ceramic Composite Intermediate Temperature Stress-Rupture Properties Significantly Improved

Morscher, G.N. and Hurst, J.

Silicon carbide (SiC) composites are considered to be potential materials for future aircraft engine parts such as combustor liners. It is envisioned that on the “hot side” (inner surface) of the combustor liner, composites will have to withstand temperatures in excess of 1200°C for thousands of hours in oxidizing environments. This is a severe condition; however, an equally severe if not more detrimental condition exists on the “cold side” (outer surface) of the combustor liner. Here, the temperatures are expected to be on the order of 800 to 1000°C under high tensile stress due to thermal gradients and attachment of the combustor liner to the engine frame (the “hot side” will be under compressive stress, a less severe stress-state for ceramics). Since these composites are non-oxides, they oxidize. The worst form of oxidation for strength reduction occurs at these intermediate temperatures where the boron nitride (BN) interphase oxidizes first, which causes the formation of a glass layer that strongly bonds the fibers to the matrix. When the fibers strongly bond to the matrix or to one another, the composite loses toughness and strength and becomes brittle.

In order to increase the intermediate temperature stress-rupture properties, modifications to the BN interphase are required. With the support of the UEET (Ultra-Efficient Engine Technology) program, significant improvements have been made over the state-of-the-art SiC/SiC composites developed during the EPM (Enabling Propulsion Material) program. Three approaches have been found to yield these improvements to the intermediate temperature stress-rupture properties: fiber-spreading, high-temperature silicon (Si)-doped BN, and “outside debonding” BN. Fibers were spread by mechanically spreading tows in the woven cloth or by heat-treating woven cloth in order to produce an insitu-BN layer on the fibers, which naturally increases the distance between neighboring fibers. High-temperature Si-doped BN has been applied as the interphase layer to woven cloth which is then stacked to fabricate SiC matrix composites. The Si-doped BN contains little oxygen (< 1 atomic percent) and approximately 7 atomic percent Si. “Outside debonding” refers to BN interphases that have been processed so as to cause interfacial debonding and sliding between the BN interphase and the SiC matrix. The interface where debonding and sliding occurs for conventional BN-interphase composites is between the BN interphase and the SiC fiber. This enables the oxidizing environment direct access to the SiC fiber and more rapid strength-reduction. “Outside debonding” interphases dramatically slows down this process since the oxidizing environment is blocked to a great extent by the relatively thick BN interphase.

It is evident that if these methods can be incorporated to new components, higher design stresses can be tolerated for the intermediate temperature regions of combustor liners. Work is continuing to combine some of these approaches and further minimize the strength-reduction that occurs at intermediate temperatures.

Improving the Pest Resistance of SiC/BN/SiC Composites

Linus U. Thomas-Ogbuji

Ceramic-matrix composites (CMCs) consisting of silicon carbide matrix reinforced with a boron nitride (BN)-coated silicon carbide (SiC) fiber are strong contenders for commercial and aerospace applications. In particular, hot sections of high-performance turbine engines in advanced aircraft and generators. They have very good mechanical properties below $\sim 600^{\circ}\text{C}$ and above $\sim 1000^{\circ}\text{C}$. Between those temperatures, however, the BN coating oxidizes easily and the oxidation of the SiC matrix is too sluggish to seal off the composite with a protective layer of silica. In that temperature interval preferential oxidation of the BN weakens and embrittles the composite. The phenomena referred to as “pest” degradation, is the focus of this work. The aim of this work is to identify the causes and remedies for pesting.

It was previously established that pesting in Hi-NicalonTM/SiC composites was caused by a layer of free carbon which undermined oxidation resistance of the BN. New work suggests that composites containing a source of carbon are prone to severe pesting, and those that are free of elemental carbon are resistant to pesting. In composites reinforced with *Nippon Carbon's* Hi-NicalonTM and Hi-Nicalon(S)TM fibers the deleterious excess free carbon comes from a stoichiometric excess within the fiber; in composites reinforced with *Dow Corning's* SylramicTM fibers, a similar carbon layer has been observed between the fiber and the BN when the fibers were sized with polyethylene oxide (PEO). However, when the SylramicTM fibers were sized with polyvinyl alcohol (PVA) free carbon was missing. Pest resistance was assessed by exposing machined samples for 100-150 h in an atmospheric burner rig at 600-1100°C, followed by a tensile fracture test to measure residual mechanical properties and characterization of the interphase microstructure. Whether the elemental carbon came from intrinsic or extrinsic sources, its presence induced the tensile strength to drop by over 50% in the burner rig, with even a more severe loss of fracture strain. A likely mechanism is burn-off of the carbon layer exposes the BN to accelerated flank attack by ambient oxidants. The BN is replaced with borosilicates that attack the fiber, and ultimately with silica that embrittles the composites by rigidly bonding components.

Thus, the study has shown that pesting in SiC/BN/SiC can be prevented, or at least reduced, by the simple measure of excluding free carbon. These studies continue, and future work will include investigation of the role that carbon may play elsewhere in the interphase region.

Effect of Environment on Stress-Rupture Behavior of a C/SiC Composite

Michael J. Verrilli, J. Douglas Kiser, Elizabeth Opila, and Anthony Calomino

Advanced reusable launch vehicles (RLV) will likely incorporate fiber-reinforced ceramic matrix composites (CMCs) in critical propulsion and airframe components. Use of CMCs is highly desirable to save weight, to improve reuse capability, and to increase performance. One of the candidate CMC materials is carbon fiber-reinforced silicon carbide (C/SiC).

In potential propulsion applications, such as turbopump rotors and nozzle exit ramps, C/SiC components will be subjected to a service cycle that includes mechanical loading under complex, high-pressure environments containing hydrogen, oxygen, and steam. Degradation of both the C fibers and the SiC matrix are possible in these environments. The objective of this effort was to evaluate the mechanical behavior of C/SiC in various environments relevant to RLV applications. Stress-rupture testing was conducted on C/SiC specimens in air and steam-containing environments. Also, the oxidation kinetics of the carbon fibers that reinforce the composite were monitored by thermogravimetric analysis (TGA) in the same environments and temperatures used for the stress-rupture tests of the C/SiC composite specimens.

Stress-rupture lives were obtained for C/SiC tested in air and in steam/argon mixtures. As is typical for most materials, lives obtained at the lower temperature (600 °C) are longer than for the high temperature (1200 °C). The effect of environment was most pronounced at the lower temperature where average test duration in steam at 600 °C was at least 30 times longer than the lives obtained in air. The 1200 °C data revealed little difference between lives of specimens tested in air and steam at atmospheric pressure.

Damage occurred during the stress-rupture testing at 600 and 1200°C in steam. Little composite damage was seen in the specimen tested at 600 °C, while damage, in the form of carbon fiber oxidation, exists in the specimen tested at 1200 °C. Similar damage was found in specimens tested in air. The TGA results revealed that the oxidation rate of the carbon fibers in the various environments correlated with the composite stress-rupture lives.

Rupture testing and strength measurements studies are ongoing to guide composite life prediction method development for C/SiC as well as to provide fundamental understanding of the damage mechanisms in ceramic matrix composites in environments relevant to future launch vehicle applications.

Thermal Cyclic Behavior of Thermal and Environmental Barrier Coatings Under High Heat Flux Conditions

Dongming Zhu, Kang N. Lee and Robert A. Miller

Environmental barrier coatings (EBCs) have been developed to protect SiC (silicon carbide)-based ceramic components in gas turbine engines from high temperature environmental attack. With continuously increasing demands for significantly higher engine operating temperature, future EBC systems must be designed for both thermal and environmental protection of the engine components in combustion gases. In particular, thermal barrier functions of EBCs become a necessity for reducing the engine component thermal loads and chemical reaction rates, thus maintaining required mechanical properties and durability of these components. The advances in thermal and environmental barrier coatings (TBCs and EBCs, respectively) development will directly impact the successful use of ceramic components in advanced engines.

In order to develop high performance coating systems, advanced test approaches must be established. In this study, a laser high heat-flux technique has been employed to investigate thermal cyclic behavior of TBCs/EBCs on SiC-reinforced SiC ceramic matrix composite substrates (SiC/SiC) under high thermal gradient and thermal cycling conditions. Because the laser heat flux test approach can monitor the coating's real-time thermal conductivity variations at high temperature, the coating thermal insulation performance, sintering and delamination can all be obtained during the thermal cycling tests.

Plasma-sprayed yttria stabilized zirconia (ZrO_2 -8wt% Y_2O_3) thermal barrier and barium strontium aluminosilicate-based environmental barrier coatings (BSAS/BSAS+mullite/Si) on SiC/SiC ceramic matrix composites were investigated in the present study. These coatings were laser tested in air under thermal gradients (the surface and interface temperatures were at approximately 1482°C and 1300°C, respectively). Some coatings specimens were also subject to alternating furnace cycling (in a 90% water vapor environment at 1300°C) and the laser thermal gradient cycling tests (in air), to investigate the water vapor effect. All cyclic tests were conducted using a 60 min hot time temperature.

The thermal conductivity of the 254 mm thick BSAS/mullite-20wt%BSAS coating system changes as a function of the cycle number. For both the laser and combined furnace-laser tested specimens, initial thermal conductivity increased considerably due to the coating sintering. However, the coating conductivity then decreased under the further testing due to coating cracking and delamination. Coating sintering and coating delamination occurred faster under the combined furnace water vapor and laser cyclic test conditions, indicating that the water vapor has a detrimental effect on coating durability. Typical failure modes and cracking morphologies of the BSAS and BSAS/mullite-20wt%BSAS two-layer coatings under the combined furnace and water vapor cycles exposure were determined. The coating failure was accelerated, by the interface pore formation in the water vapor environments, and by subsequent coating delamination under the laser thermal gradient cyclic testing.

For a ZrO_2 -8wt% Y_2O_3 /BSAS/BSAS+mullite/Si multi-layered coating system tested under thermal gradient cyclic conditions, thermal conductivity showed a similar trend with the cycle numbers as observed for the BSAS/mullite-20wt%BSAS coating systems. The coating sintering induced initial conductivity increase and subsequently coating cracking-delamination induced conductivity decrease were determined. However, the combined effects of the thermal expansion mismatch between the different coating layers and the substrate, along with the sintering shrinkage of the ceramic coatings, resulted in substantial wedge-shape surface cracking and coating delaminations.

Ceramic Propellant Injectors

Andrew J. Eckel

Ceramic propellant injectors offer the potential for order of magnitude weight reductions compared to conventional metallic injectors and may enable some NASA missions. Injectors constructed of ceramic materials have the inherent advantages of being lighter weight, more erosion resistant, and capable of higher temperature operation than current metallic designs. The use of ceramics may facilitate new designs for a broad range of combustion devices in aero and space applications. In a joint project involving the Ceramics Branch and the Combustion Branch, a rocket propellant injector faceplate has been designed and fabricated using laminated object manufacturing and standard ceramic processing. Preliminary bench test results have proven successful.

Light-Weight, Actively-Cooled Ceramic Matrix Composite Thrustcells Successfully Tested in Rocket Combustion Lab

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In a joint effort between NASA GRC and NASA Marshall, regeneratively cooled ceramic matrix composite (CMC) thrustcells were developed and successfully tested in the Rocket Combustion Lab at NASA GRC. Cooled CMCs offer the potential for substantial weight savings over more traditional metallic parts. Two CMC concepts were investigated. In the first of these concepts an innovative processing approach was utilized by Hyper-Therm, Inc which allowed woven CMC coolant containment tubes to be incorporated into the complex thruster design. In this unique design, the coolant passages had varying cross-sectional shape but maintained a constant cross-sectional area along the length of the thruster. These thrusters were silicon carbide matrix composites reinforced a silicon carbide fibers.

The second concept, which was supplied by Ceramic Composites, Inc (CCI), utilized copper cooling coils surrounding a carbon fiber reinforced carbon matrix composite. In this design, a protective gradient coating was applied to the inner thruster wall. CCI's method of incorporating the coating into the fiber and matrix eliminated the spallation problem often observed with thermal barrier coatings during hot-fire testing. The focus of the testing effort was on screening of the CMC materials capabilities as well as evaluation of the thermal barrier coatings or fiber/matrix interfacial coating performance. Both concepts were hot-fire tested in gaseous O_2/H_2 environments. The test matrix included oxygen to fuel ratios ranging from 1.5 to 7 with chamber pressures up to 400 psi. Steady state Internal wall temperatures in excess of 4300°C were measured in-situ for successful 30 second test runs.

Environment Conscious Ceramics (Ecoceramics) Technology Wins 2001 R&D 100 Award

Mrityunjay Singh

Since the dawn of human civilization, there has always been a delicate balance between the various activities of mankind that utilize resources while expanding the human frontiers and the need to have minimum influence on the ecosystem. The first two hundred years of the industrial revolution essentially solved the problem of production. However, the massive production of goods also generated tremendous amounts of by-products and wastes. In the new millennium, in order to sustain a healthy life in harmony with nature, it will be extremely important to develop various materials, products, and processes that minimize any harmful influence on the environment.

Environment conscious ceramics (Ecoceramics) are a new class of materials, which can be fabricated with renewable resources (wood) and wood waste material (wood sawdust). Wood is a “lignocellulosic” material formed by the photosynthetic reaction within the needles or leaves of trees. The photosynthesis process uses sunlight to take carbon dioxide from air and convert it into oxygen and organic materials. Wood has been known to be one of the best and most intricate engineering materials created by nature and known to mankind. In addition, natural woods of various types are available throughout the world. On the other hand, wood saw dusts are generated in abundant quantities by sawmills. The environment conscious ceramic materials, fabricated via the pyrolysis and infiltration of natural wood-derived preforms, have tailorable properties with numerous potential applications. The experimental studies conducted to date on the development of materials based on biologically derived structures indicate that these materials behave like ceramic materials manufactured by conventional approaches. These structures have been shown to be quite useful in producing porous or dense materials having various microstructures and compositions.

Wood pieces are dried in an oven and pyrolyzed in a furnace up to 1000°C in a flowing argon atmosphere to create carbonaceous preforms. The weight and dimensional changes were recorded after pyrolysis. The pyrolyzed preforms were infiltrated with silicon in a graphite element furnace under vacuum. The infiltration time and temperature depend on the melting point of the infiltrants and dimensions and properties of the preforms. For silicon infiltration, porous preforms were infiltrated at 1450°C for 30 minutes. A wide variety of wood specimens (softwood and hardwood) and wood saw dusts were used for the fabrication of carbonaceous preforms. The ecoceramic technology has been used to fabricate complex shaped parts from the machined wood or carbon specimens. Detailed thermomechanical characterization of a wide variety of silicon carbide-based ecoceramics is underway.

Strength and Fracture Toughness of Solid Oxide Fuel Cell (SOFC) Electrolyte Material Improved

Bansal, N.P. and Choi, S.R.

Solid oxide fuel cells (SOFC) are being developed for various applications in the automobile, power generation, and aeronautics industries. More recently, NASA is exploring the possibility of using SOFCs for aero-propulsion under its Zero Carbon Dioxide Emission Technology (ZCET) Program. Ytria-stabilized zirconia (10YSZ) is a very good anionic conductor at high temperatures, and is therefore used as an oxygen solid electrolyte in SOFC. However, it has high thermal expansion coefficient, low thermal shock resistance, low fracture toughness and poor mechanical strength. For aeronautic applications, the thin ceramic electrolyte membrane of the SOFC needs to be strong and tough. At NASA, we have been investigating the possibility of enhancing the strength and fracture toughness of the 10YSZ electrolyte without degrading its electrical conductivity to an appreciable extent.

We have recently demonstrated that the addition of alumina to zirconia electrolyte increases its strength as well as its fracture toughness. Zirconia-alumina composites containing 0-30 mole percent of alumina were fabricated by hot pressing. The hot pressing procedure has been developed and various hot pressing parameters optimized resulting in dense and crack-free panels of composite materials. Cubic zirconia and α -alumina were the only phases detected indicating no chemical reaction between the constituents during hot pressing at elevated temperatures. Flexure strength (s_f) and fracture toughness (K_{IC}) of the various zirconia-alumina composites were measured at room temperature as well as at 1000 °C in air. Both the properties showed systematic improvement with amount of alumina addition at room temperature and at 1000 °C.

Use of these modified electrolytes with improved strength and fracture toughness should prolong the life and enhance the performance of SOFC in aeronautics and other applications.

Novel Molecular Architectures for Improved Solid Polymer Electrolytes for Lithium Polymer Batteries

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Lithium based polymer batteries for aerospace applications need the ability to operate in temperatures ranging from -70°C to $+70^{\circ}\text{C}$. Current state of the art solid polymer electrolytes (based on amorphous polyethylene oxide, PEO) have acceptable ionic conductivities (10^{-4} to 10^{-3} S/cm) only above 60°C . Higher conductivity can be achieved in the current systems by adding solvent or plasticizers to the solid polymer to improve ion transport. However, this can compromise dimensional and thermal stability of the electrolyte, as well as compatibility with electrode materials. Our objective in the PERS program is to develop new electrolytes having unique molecular architecture, and/or novel ion transport mechanisms leading to good ionic conductivity at room temperature and below with no solvent or plasticizers.

It is widely held that ionic conductivity is highest for amorphous (non-crystalline) polymers with low glass transition temperatures. This is thought to be because strong coulombic forces and low free volume trap the ions in the crystalline regions. However, promising new approaches to less temperature dependent ionic conductivity in solid polymers include ways of introducing free volume and short-range order if not crystallinity into the system. Some of these approaches include Langmuir-Blodgett films, liquid crystals, and self-assembling monolayers.

We are combining several of these approaches to investigate new polymers with novel architectures for stable, processable polymer electrolytes with enhanced ionic conductivity over a wide range of temperatures. One approach under investigation in-house is a series of rod-coil block copolymers in which rigid polyimide rods alternate with very flexible, short PEO strands. Because of the incompatibility between the rods and coils, the blocks would tend to phase separate as much as possible. This leads to formation of nanoscale channels of ionically conducting PEO alternating with the rigid polyimide rods. The rod regions form mechanical support for conducting PEO coils, giving films with both good conductivity and mechanical integrity.

The rod-coil polyimides doped with lithium salts form rubbery films having glass transition temperatures around -50°C . Polymers with room temperature conductivities as high as 2.3×10^{-5} S/cm have been synthesized so far. This is almost an order of magnitude better than measured state of the art PEO. Rod-coil polymers are easily cast from 40 weight percent solutions and cured into the flexible, solvent-free films by heating to 200°C . The films could be cast directly onto electrode substrates or handled as free standing films, offering flexibility in battery fabrication.

High T_g Polyimides for Reusable Launch Vehicle Applications

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Kathy Chuang and Cory P. Ardent

Polyimide composites have been traditionally used for high temperature applications in aircraft engines at temperatures up to 550 °F (288 °C) for thousands of hours. However, as NASA shifts its focus towards the development of advanced Reusable Launch Vehicles (RLV), there is an urgent need for light-weight polymer composites that are capable of sustaining 600-800 °F (315 - 427 °C) for short excursions (hundreds of hours). To meet critical vehicle weight targets, it is essential to use light-weight high temperature polymer matrix composites in propulsion components such as turbopump housings, ducts, engine supports and struts. Composite materials in RLV components will experience fast heating rates during launch and reentry. Conventional composites, consisting of layers of fabric or fiber reinforced lamina, would either blister or encounter catastrophic delamination under high heating rates above 300 °C. This blistering and delamination are the result of a sudden volume expansion within the composite due to the release of absorbed moisture and gases generated by the degradation of polymer matrix. Researchers at GRC and Boeing, Long Beach, have recently demonstrated a successful approach of preventing this delamination through the use of 3-D stitched composites fabricated by resin infusion.

Concentrated solutions of a series of GRC developed high T_g polyimides (T_g = 370-420 °C) have been successfully infused into stitched carbon fabric preforms to prepare composites. DMBZ-15 stitched composites display the highest open-hole compression strength at 650 °F (343 °C) of all resins tested while HFBZ composites exhibit the highest interlaminar shear strength at 650 °F (343 °C). HFPE composites have shown excellent thermo-oxidative stability as they retain 50% of their mechanical properties after isothermal aging at 550 °F (288 °C) for 2000 hours and maintain 60% of their room temperature mechanical properties at 650 °F (343 °C). The mechanical properties of these high T_g polyimide composites far exceed the performance of a leading commercial high temperature bismaleimide, BMI 5270. These stitched composites hold promise of performing at high temperatures without delamination under high moisture and high heating rate conditions encountered in many RLV applications.

Polymer/ Silicate Nanocomposites for Improved Thermal Stability and Barrier Properties

Sandi Campbell

The nano-scale reinforcement of polymers is becoming an attractive means of improving polymer properties and stability. Polymer- silicate nanocomposites are a relatively new class of materials with phase dimensions typically on the order of a few nanometers. Because of their nanometer size features, nanocomposites possess unique properties typically not shared by more conventional composites. Polymer-layered silicate nanocomposites can attain a certain degree of stiffness, strength and barrier properties with far less ceramic content than comparable glass or mineral reinforced polymers.¹ Reinforcement of existing and new polyimides by this method offers an opportunity to greatly improve existing polymer properties without altering current synthetic or processing procedures.

Highly crosslinked, thermally stable, thermosetting polymers have not been extensively researched as nanocomposite matrix materials. By dispersing a layered silicate into a PMR-15 matrix, there is the potential to increase the use temperature and the high temperature performance of the polymer. Nanocomposite synthesis typically requires modification of the silicate interlayer with an organic material to improve the compatibility between the clay and the polymer. An understanding of the effects of the silicate on the melt viscosity and the crosslinking of the PMR-15 oligomers is important to the selection of a silicate-organic modification system which will optimize the benefits of the nano-scale reinforcement.

Recent efforts at the NASA Glenn Research Center have led to an organically modified silicate which on dispersion in a PMR-15 matrix, leads to a nanocomposite with up to a 12% increase in thermal oxidative stability. Utilization of the PMR-15 nanocomposite as a matrix to a polymer carbon fabric (T650-35) composite increases the composite thermal stability by 25% in comparison to a neat PMR-15 matrix composite.

An organically modified silicate was also dispersed in a thermoplastic polyimide matrix. The silicate was modified with protonated amines of varying lengths and architecture and several nanocomposites were prepared. Water and acetone absorption into the neat resin and the nanocomposites was investigated. The absorption of acetone into the nanocomposite samples was decreased in comparison to the neat polymer by 30% to 47%, after 28 hours. In water, absorption was decreased by 10% to 22% after 32 hours. Hydrogen permeability testing of these material results in a 10% to 20% decrease in permeability. The effectiveness of the nanocomposite in decreasing absorption or permeation was dependent on the silicate modification.

The mechanical properties of both the thermosetting and thermoplastic polyimide matrix nanocomposites are currently being evaluated.

NASA GRC/AADC Collaboration Optimizes Erosion Coatings for Inlet Guide Vanes

James K. Sutter, George Leissler, and Richard Horan

There is a need for lightweight, durable materials and structures to enable reduction in weight for propulsion systems. Polymer matrix composites (PMC) are very attractive materials for aerospace applications because of their high strength to weight ratio relative to that of metals. Unfortunately, PMCs are limited to applications where they are not exposed to high temperature oxidizing atmospheres and/or particulates from ingested air. This is because oxidation and erosion occur on the surface leading to weight loss, nodulation and/or cracking on the surface, and a decline of mechanical properties over time.

Prior research has shown that oxidation can be slowed by application of metallic or ceramic coatings. However, there remains a need for erosion resistant coatings that protect a PMC from high velocity particulates in the engine flow path and, thereby extend the life of the composite. Polymer composites are heavily damaged without an erosion coating because they are not as hard as metallic engine structures.

The effectiveness and life of the coatings is dependent on their inherent properties as well as the interaction between the coating and the PMC. Since polymers, in general, have high thermal expansion coefficients compared to metals and ceramics, failure of the coatings often occurs at this interface. The objective of this research is to develop strategies to improve this interface and tailor overcoats for erosion resistance. The bondcoat was developed at NASA GRC and comprised of zinc blended with polyimides to improve the compatibility between the PMC and the topcoat. Initial coating trials at AADC produced vanes that had poor bonding between the top and bondcoats. Subsequently, NASA GRC successfully demonstrated that high quality plasma sprayed erosion coatings were applied to these guide vanes. Inlet guide vanes from AE 3007 engines fiber composites were coated using a coating system comprised of a bondcoat and a hard topcoat. Optimization of the plasma spray process has led to future erosion testing in gas turbine engine environments.